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A.N. Zelikman, O.E. Krein, and G.V. Samsonov

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METALLURGY OF RARE METALS

TRANSLATED FROM RUSSIAN

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A. N. Zelikman, O. E. Krein, and G. V. Samsonov

METALLURGY OF RARE METALS

(Metallurgiya redkikh metallov)

Second Edition, Revised and Enlarged
Edited by L. V. Belyaevskaya

Approved by the Ministry of Higher and Secondary Specialized Education of the USSR as a textbook for students of nonferrous metallurgy

Izdatel'stvo Metallurgiya
Moskva 1964

Translated from Russian

Israel Program for Scientific Translations
Jerusalem 1966

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NASA TT F-359
TT 65-50137

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THE NATIONAL SCIENCE FOUNDATION, WASHINGTON, D. C.

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Israel Program for Scientific Translations Ltd.
IPST Cat. No. 1455

Translated by A. Aladjem, Chem. Eng.

Printed in Jerusalem by S. Monson
Binding: Wiener Bindery Ltd., Jerusalem

Price: $ 8.12

Available from the
U. S. DEPARTMENT OF COMMERCE
Clearinghouse for Federal Scientific and Technical Information
Springfield, Va. 22151

VI/18/3.5

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EXPLANATORY LIST OF ABBREVIATIONS OF U. S. S. R. INSTITUTIONS AND JOURNALS APPEARING IN THIS TEXT

Abbreviation	*Full name (transliterated)*	*Translation*
AN KazSSR	Akademiya Nauk Kazakhskoi SSR	Academy of Sciences of the Kazakh SSR
Atomizdat	Izdatel'stvo Gosudarstvennogo Komiteta Soveta Ministrov SSSR po Ispol'zovaniyu Atomnoi Energii	Publishing House of the State Committee of the Council of Ministers of the USSR on Uses of Atomic Energy
DAN SSSR	Doklady Akademii Nauk SSSR	Transactions of the Academy of Sciences of the USSR
Fizmatgiz	Gosudarstvennoe Izdatel'stvo Fiziko-Matematicheskoi Literatury	State Publishing House of Physical and Mathematical Literature
GDR	Germanskaya Demokraticheskaya Respublika	German Democratic Republic
Giredmet	Gosudarstvennyi Nauchno-Issledovatel'skii i Proektnyi Institut Redkometallicheskoi Promyshlennosti	State Scientific-Research and Planning Institute of Rare-Metals Industry
Goskhimizdat	Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatel'stvo Khimicheskoi Literatury	State Scientific and Technical Publishing House of Chemical Literature
Izd. AN SSSR	Izdatel'stvo Akademii Nauk SSSR	Publishing House of the Academy of Science of the USSR
Izv.	Izvestiya	Bulletin
Kirg SSR	Kirgizskaya SSR	Kirgiz SSR
LGU	Leningradskii Gosudarstvennyi Universitet	Leningrad State University
Mekhanobr	Nauchno-Issledovatel'skii Institut Mekhanicheskoi Obrabotki Poleznykh Iskopaemykh	Scientific Research Institute for Mechanical Concentration of Minerals

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Abbreviation	Full name (transliterated)	Translation
MGU	Moskovskii Gosudarstvennyi Universitet	Moscow State University
NTOTsM	Nauchno-tekhnicheskii Otdel Tsvetnoi Metallurgii	Scientific and Technical Division of Nonferrous Metallurgy
RZh	Referativnyi Zhurnal	Abstract Journal
SO AN SSSR	Sibirskoe Otdelenie Akademii Nauk SSSR	Siberian Department of the Academy of Sciences of the USSR
TsNIIChM	Tsentral'nyi Nauchno-Issledovatel'skii Institut Chernoi Metallurgii imeni J. P. Bardina	Central Scientific-Research Institute of Ferrous Metallurgy im. J. P. Bardin
TsNIITsM	Vsesoyuznyi Tsentral'nyi Nauchno-Issledovatel'skii Institut Tsvetnoi Metallurgii	All-Union Central Scientific Research Institute of Nonferrous Metallurgy
UkrSSR	Ukrainskaya SSR	Ukrainian SSR
VINITI	Vsesoyuznyi Institut Nauchnoi i Tekhnicheskoi Informatsii	All-Union Institute for Scientific and Technical Information
VUZ	Vysshee Uchebnoe Zavedenie	Higher Educational Institution
ZhFKh	Zhurnal Fizicheskoi Khimii	Journal of Physical Chemistry
ZhNKh	Zhurnal Neorganicheskoi Khimii	Journal of Inorganic Chemistry
ZhOKh	Zhurnal Obshchei Khimii	Journal of General Chemistry
ZhPKh	Zhurnal Prikladnoi Khimii	Journal of Applied Chemistry

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FOREWORD

Rare metals play an important role in the development of major branches of industry, such as vacuum equipment, semiconductor electronics, nuclear power and rocket production, as well as in the production of special steels and hard, refractory and corrosion-resistant alloys.

Rapid development and improvement in the production of rare metals took place in the ten years which have elapsed since the publication of the first edition of this book. These ten years have witnessed the beginning of large-scale production of titanium, zirconium, and germanium, and a significant increase in the production volume; new, improved methods for the separation and purification of metals and compounds (ion-exchange, extraction, crystallization methods) as well as arc and electron-beam melting processes for metals were developed. This made it necessary to rewrite most of this book.

In view of the growing importance of the lanthanides and rhenium, chapters on these metals were also included. At the same time, we decided to dispense with the chapters on lead and antimony, since these are not usually listed as rare metals. In describing the metallurgy of each metal, much attention was paid to its physicochemical nature and to the practical operations involved in the main technological processes for the production of its chemical compounds and of the pure metal.

This book is a textbook for students specializing in the metallurgy of the rare metals. It is assumed that the student is familiar with the physicochemical fundamentals of metallurgy, ore dressing, metallurgical furnaces, and processes and apparatus used in extractive metallurgy. The description of standard equipment (leaching apparatus, thickeners, filters, comminution installations, etc.) has accordingly been omitted. The references are grouped together at the end of the book.

Chapters I, III, IV, V, VI, VII, VIII, and XII were written by A. N. Zelikman, Chapters II, IX, X, and XI — by A. N. Zelikman and O. E. Krein, and Chapters XIII and XIV — by G. V. Samsonov.

The authors wish to thank their many colleagues at the State Institute of Rare Metals (Giredmet). They are especially grateful to Professor G. A. Meerson for his valuable advice and help in the preparation of the manuscript and Associate Professor L. V. Belyaevskaya, the editor of this book.

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INTRODUCTION

At the beginning of the 20th century, certain chemical elements found important industrial applications for the first time. This group of elements is known as "rare elements" or, in a more narrow sense, "rare metals".

As may be seen in Table 1 (in which the rare metals appear in bold-face frames) the "rare metals" group comprises metals in all groups of the periodic table. Their physicochemical properties are accordingly very different, and the rare metals group comprises those metals which for a number of reasons have only recently found commercial use.

The main reason for it is that most rare metals were only discovered at the end of the 18th and in the 19th centuries. At the same time, their scarcity and the fact that many of the rare metals are widely dispersed over the Earth's crust, as well as the difficulties encountered in the extraction and purification of some of them, also interfered with their industrial utilization.

Table 2 (compiled by Academicians V. I. Vernadskii and A. E. Fersman) shows the use of chemical elements by man, in various historical periods. The use of all metals in the "rare metals" group dates from the 19th and 20th centuries.

Thus, the concept "rare metal" originally referred to metals which had little or no technological use. In our own time, however, many rare metals are extensively used in modern technology. The very existence of a number of branches of technology would be unthinkable without the use of rare metals. Of the 70 metals (listed in Table 3) in production at the present time, forty-one belong to the rare-metals groups. Thus, the "rare-metals" group is not a scientific classification but has a historical meaning.

It is a common error to associate the term "rare metal" with a low abundance of the element in nature. To correct this misconception, we shall give some recent data on the abundance of elements in the Earth's crust. Proceeding from analytical data, geochemists calculated the composition of the Earth's crust, down to a depth of 16 km. The first tables showing the composition of the Earth's crust were compiled in 1889 by the American scientist F. Clark. Their accuracy was subsequently improved. An important contribution to the study of the abundance of elements in the Earth's crust was made by the Soviet scientists, V. I. Vernadskii, A. E. Fersman, V. G. Khlopin, and A. P. Vinogradov.

In accordance with the suggestion of A. E. Fersman, the average contents of the elements in the Earth's crust are designated as "clarkes".

The average contents of the elements, in weight percent, are shown in Table 4. The first row includes elements whose abundance is above 10%, the second — those with abundances between 1 and 10%, the third — from 0.1 to 1%, etc. It is evident that the distribution of elements in

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TABLE 1

PERIODIC TABLE OF ELEMENTS

	I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII	0
1	H 1 Hydrogen 1,00797																	He 2 Helium 4,0026
2	Li 3 Lithium 6.939	Be 4 Beryllium 9.0122	B 5 Boron 10.811											C 6 Carbon 12.0115	N 7 Nitrogen 14.0067	O 8 Oxygen 15.934	F 9 Fluorine 18.9984	Ne 10 Neon 20.183
3	Na 11 Sodium 22.9898	Mg 12 Magnesium 24.312	Al 13 Aluminum 26.9815											Si 14 Silicon 28.086	P 15 Phosphorus 30.9738	S 16 Sulfur 32.064	Cl 17 Chlorine 35.453	A 18 Argon 39.948
4	K 19 Potassium 39.102	Ca 20 Calcium 40.08	Sc 21 Scandium 44.956	Ti 22 Titanium 47.90	V 23 Vanadium 50.942	Cr 24 Chromium 51.996	Mn 25 Manganese 54.9381	Fe 26 Iron 55.847	Co 27 Cobalt 58.9332	Ni 28 Nickel 58.71	Cu 29 Copper 63.54	Zn 30 Zinc 65.37	Ga 31 Gallium 69.72	Ge 32 Germanium 72.59	As 33 Arsenic 74.9216	Se 34 Selenium 78.96	Br 35 Bromine 79.909	Kr 36 Krypton 83.80
5	Rb 37 Rubidium 85.47	Sr 38 Strontium 87.63	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.22	Nb 41 Niobium 92.906	Mo 42 Molybdenum 95.94	Tc 43 Technetium [97]	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.4	Ag 47 Silver 107.870	Cd 48 Cadmium 112.41	In 49 Indium 114.82	Sn 50 Tin 118.69	Sb 51 Antimony 121.75	Te 52 Tellurium 127.60	I 53 Iodine 126.9044	Xe 54 Xenon 131.30
6	Cs 55 Cesium 132.905	Ba 56 Barium 137.34	La 57 Lanthanum 138.91	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.948	W 74 Tungsten 183.85	Re 75 Rhenium 186.2	Os 76 Osmium 190.2	Ir 77 Iridium 192.2	Pt 78 Platinum 195.09	Au 79 Gold 196.967	Hg 80 Mercury 200.59	Tl 81 Thallium 204.37	Pb 82 Lead 207.19	Bi 83 Bismuth 208.980	Po 84 Polonium [210]	At 85 Astatine [210]	Rn 86 Radon [222]
7	Fr 87 Francium [223]	Ra 88 Radium [226]	Ac 89 Actinium [227]															

LANTHANIDES (RARE-EARTH ELEMENTS)

Ce 58 Cerium 140.12	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium [147]	Sm 62 Samarium 150.35	Eu 63 Europium 151.96	Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.924	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.930	Er 68 Erbium 167.26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutecium 174.97

ACTINIDES

Th 90 Thorium 232.038	Pa 91 Protactinium 231	U 92 Uranium 238.03	Np 93 Neptunium [237]	Pu 94 Plutonium [242]	Am 95 Americium [243]	Cm 96 Curium [247]	Bk 97 Berkelium [247]	Cf 98 Californium [249]	Es 99 Einsteinium [254]	Fm 100 Fermium [253]	Md 101 Mendelevium [256]	No 102 Nobelium [253]?	Lw 103 Lawrencium [257]

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the Earth's crust is very nonuniform. The nine most abundant elements account for 98.13% of the total amount of matter in the Earth's crust, i.e., the remaining 83 elements account for only 1.87% of it.

TABLE 2

The increasing use of chemical elements (both in the free state and as compounds)

Period	Elements	Total number of elements
Ancient times	N, Al, Fe, Au, K, Ca, O, Si, Cu, Na, Sn, Hg, S Pb, Ag, C, Cl, Zn, Sb	19
Up to the 18th century	In addition to the above: As, Mg, Bi, Co, B, Ni, P	26
The 18th century	" " " " " H, Pt, Ir, J	30
The 19th century	" " " " " Ba, Br, V, W, Cd, Mn, Mo, Os, Pd, Ra, Sr, Ta, F, Th, U, Cr, Zr and lanthanides (15 elements)	62
20th century up to 1915	" " Ne, Li, He, Ti, Ac, Ru, Rh	69
20th century up to 1932	lanthanides (15 elements) Be, Ar, Ga, Se, Rb, Y, In, Te, Nb, Hf, Re, Tl, Cs	82
Up to 1957	Ge, Po, Sc	

Note: the metals used since ancient times are underlined; the rare metals are boxed in.

TABLE 3

Metals produced today* (the rare metals are underlined)

Group in the periodic table	Elements	Total number	Rare metals
I	Li, Na, K, Rb, Cs, Cu, Ag, Au	8	3
II	Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg	9	2
III	Al, Sc, Y, La, Ga, In, Tl	7	6
IV	Ti, Zr, Hf, Ge, Sn, Pb	6	4
V	V, Nb, Ta, As, Sb, Bi	6	3
VI	Cr, Mo, W, Se, Te, Po	6	5
VII	Mn, Re	2	1
VIII	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt	9	—
Lanthanides	From No. 58 (Ce) to No. 71 (Lu)	14	14
Actinides	Th, U, Pu	3	3
	Total ..	70	41

* Produced in the form of metal, alloy or chemical compound.

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TABLE 4

Average chemical composition of the Earth's crust (according to Vinogradov)
(thickness 16 km, excluding the atmosphere and the ocean)

Decade	Abundance limits, wt%	Chemical elements and their occurrence in wt%
I	10—50	O 47.2; Si 27.6
II	1—10	Al 8.80; Fe 5.10; Ca 3.60; Na 2.64; K 2.60; Mg 2.10
III	$1—10^{-1}$	Ti 0.60; H (0.15); C 0.10
IV	$10^{-1}—10^{-2}$	Mn 0.09; P 0.08; S 0.05; Ba 0.05; Cl 0.045; Sr 0.04; Rb 0.031; F 0.027; Zr 0.020; Cr 0.02; V 0.015; Cu 0.01; N 0.01
V	$10^{-2}—10^{-3}$	Ni $8 \cdot 10$; Li $6.5 \cdot 10^{-3}$; Zn $5 \cdot 10^{-3}$; Ce $4.5 \cdot 10^{-3}$; Sn $4 \cdot 10^{-3}$; Co $3 \cdot 10^{-3}$; Y $2.8 \cdot 10^{-3}$; Nd $2.5 \cdot 10^{-3}$; La $1.8 \cdot 10^{-3}$; Pb $1.6 \cdot 10^{-3}$; Ga $1.5 \cdot 10^{-3}$; Nb $1 \cdot 10^{-3}$; Gd $1 \cdot 10^{-3}$
VI	$10^{-3}—10^{-4}$	Th $8 \cdot 10^{-3}$; Cs $7 \cdot 10^{-4}$; Pr $7 \cdot 10^{-4}$; Sm $7 \cdot 10^{-4}$; Ge $7 \cdot 10^{-4}$; Be $6 \cdot 10^{-4}$; Sc $6 \cdot 10^{-4}$; As $5 \cdot 10^{-4}$; Dy $4.5 \cdot 10^{-4}$; Er $4 \cdot 10^{-4}$; Yb $3 \cdot 10^{-4}$; U $3 \cdot 10^{-4}$; Tl $3 \cdot 10^{-4}$; Mo $3 \cdot 10^{-4}$; Hf $3.2 \cdot 10^{-4}$; B $3 \cdot 10^{-4}$; Br $1.6 \cdot 10^{-4}$; Ho $1.3 \cdot 10^{-4}$; Eu $1.2 \cdot 10^{-4}$; W $1 \cdot 10^{-4}$; Lu $1 \cdot 10^{-4}$
VII	$10^{-4}—10^{-5}$	Tu $8 \cdot 10^{-5}$; Se $6 \cdot 10^{-5}$; Cd $(5 \cdot 10^{-5})$; Sb $(4 \cdot 10^{-5})$; I $(3 \cdot 10^{-5})$; Bi $(2 \cdot 10^{-5})$; Ag $(1 \cdot 10^{-5})$; In $(1 \cdot 10^{-5})$
VIII	$10^{-5}—10^{-6}$	Hg $7 \cdot 10^{-6}$; Os $5 \cdot 10^{-6}$; Pd $1 \cdot 10^{-6}$; Te $(1 \cdot 10)^{-6}$
IX	$10^{-6}—10^{-7}$	Ru $(5 \cdot 10^{-7})$; Pt $5 \cdot 10^{-7}$; Au $5 \cdot 10^{-7}$; Rh $1 \cdot 10^{-7}$; Re $1 \cdot 10^{-7}$; Ir $1 \cdot 10^{-7}$
X	less than 10^{-9}	Ac $(6 \cdot 10^{-10})$; Ra $1 \cdot 10^{-10}$; Pa $1 \cdot 10^{-10}$; Po $(2 \cdot 10^{-14})$; Pu $1 \cdot 10^{-15}$; Rn $(7 \cdot 10^{-16})$

Table 4 also shows that the abundance of most rare elements is low. However, many of the rare metals are much more abundant than metals known to man for a long time. For instance, titanium occupies the ninth place in the order of abundance; zirconium, vanadium, lithium, cerium and some other rare metals are more abundant than commonly used metals such as lead, arsenic, tin, mercury, silver and gold.

Moreover, some metals are regarded as very rare because of the manner in which they are dispersed, i. e., because they do not form minerals or deposits. For example, the concentration of gallium in the Earth's crust is higher than the concentrations of antimony, arsenic and mercury.

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However, gallium does not occur as minerals but is found in the lattices of other minerals, while antimony, arsenic and mercury form minerals and deposits, i. e., occur in a more concentrated form and thus appear to be more abundant.

A low abundance in the Earth's crust, therefore, is not a property of all the rare metals, but only of most of them.

Classification of rare metals

Rare metals are usually classified in five groups (Table 5), the classification being based on similarities in physicochemical properties, methods of extraction and production of the metals, and some other characteristics.

TABLE 5

Technological classification of the rare metals

Group in the periodic table	Elements	Technological classification
I	Lithium, rubidium, cesium	Light rare metals
II	Beryllium	
IV	Titanium, zirconium, hafnium	Refractory rare metals
V	Vanadium, niobium, tantalum	
VI	Molybdenum, tungsten	
VII	(Rhenium)*	
III	Gallium, indium, thallium	Dispersed rare metals
IV	Germanium	
VI	Selenium, tellurium	
VII	*Rhenium*	
III	Scandium, yttrium, lanthanum and lanthanides (14 elements from cerium to lutecium)	Rare earth rare metals
II	Radium	Radioactive rare metals
III	Actinium and actinides (thorium, protactinium, uranium and transuranium elements)	
V	Polonium	

* Rhenium is a typical dispersed element but because of its properties it may also be classified as a refractory metal.

A description of these groups is given below.

Light rare metals. This group comprises the metals in Groups I and II of the periodic table (except radium). They have a low density (lithium 0.53, beryllium 1.85, rubidium 1.55, and cesium 1.87 g/cm^3) and are very reactive. Their chemical compounds (oxides, chlorides) are very stable and are reduced to the metal only with difficulty.

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Like nonferrous light metals (aluminum, magnesium, calcium) light rare metals are prepared by electrolysis of their molten salts or by reduction with other metals.

Refractory rare metals. The general physicochemical properties of these metals are determined by their place in the periodic system [sic]. All are transition elements in Groups IV, V, and VI of the periodic table in which the *d*-electron sub-levels are being filled.

This feature of their atomic structure determines many of their physical and chemical properties. They are refractory (their melting points lie between 1660° for titanium and 3400° for tungsten), they are harder than other metals, and they have a high resistance to corrosion.

They may display several valencies, which accounts for the wide variety of their compounds.

All refractory metals form refractory, hard, chemically stable compounds with a number of nonmetals. Of these compounds, the carbides, nitrides, borides, and silicides have important commercial uses.

Because of the high melting point of the refractory metals, they are extensively produced by sintering methods; arc and electron-beam melting methods have been recently developed for some of them.

Because of the similarity in the properties of the refractory metals, they have many common uses. Thus, all refractory metals are used as alloys with steel and as carbides in hard alloys. Many refractory metals are used in electrical technology and in vacuum equipment manufacture.

Dispersed rare metals. All these metals occur in a dispersed state in the Earth's crust. Most elements in this group do not form separate minerals (or else such minerals are rare).

The dispersed elements are usually found as isomorphous admixtures in very small concentrations in the lattices of other minerals, and are extracted as by-products from the wastes formed in metallurgical and chemical processing.

Thus, gallium is found in aluminum minerals (bauxites and others) and is extracted from the intermediate and waste products of aluminum processing; indium, thallium, and germanium are often encountered in zinc blende and other sulfide minerals and are extracted as by-products during processing of sulfide ores. Germanium is often found in coals and is extracted from coal wastes. Rhenium occurs in molybdenum ores and is obtained as a by-product of the processing of molybdenum raw materials.

Thus, scattered metals are produced from a wide variety of raw materials, including dust from furnaces used in calcination, slurries from copper refining plants, dusts and cakes from zinc-lead industry, slurries from sulfuric acid plants, coal ash, etc. The production of these metals is closely related to the metallurgy of the common nonferrous metals.

The rare earths (lanthanides). The similarity of the physicochemical properties of the lanthanides (from cerium No. 58 to lutecium No. 71) is attributed to the similar structure of the outer electron shells of their atoms; the elements in the lanthanide series correspond to the filling of the inner 4*f*-shell. The elements lanthanum, scandium, and yttrium which belong to Group III and which are usually included in the lanthanide

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group have properties similar to those of the lanthanides. The lanthanides always occur together in ores; in the first stages of processing they are isolated as a mixture of oxides or other compounds. Interest has recently been exhibited in the isolation of the individual lanthanides. The difficult problem of the separation of lanthanide metals has now been satisfactorily solved.

Radioactive rare metals. This group comprises the naturally radioactive elements: polonium, radium, actinium, and the actinides (thorium, protactinium, uranium, and the artificially produced transuranium elements — neptunium, plutonium, etc.). The technology of these metals, the methods of their handling and their use are determined to a great extent by their radioactivity.

In the actinide series, the elements are formed by successive addition of electrons to the inner 5 *f*-shell.

In this respect, the actinides resemble the lanthanides.

The natural radioactive elements occur together in ores. They are often accompanied by lanthanides.

Both natural and artificial radioactive elements play an important role in atomic power production.

Certain features of the production of rare metals from ores

The technological processes used in the metallurgy of rare metals depend on the nature of the raw material, the physicochemical properties of the metals, and the standards required in commercial production.

1. The ores containing rare metals are usually lean ores. Hence, the enrichment of the ores is of particular importance. The rare metal ores often have a complex composition. The following ores may be taken as an example: tungsten-molybdenum; titanium-niobium-tantalum lanthanide-containing ores; uranium-vanadium; lithium-cesium; tungsten-tin; zirconium-niobium and other ores. Moreover, as has been mentioned above, some of the rare metals often occur at negligible concentrations in ores and in the wastes of ferrous and nonferrous metal processing and of chemical industry. As a result, multiple processing of raw materials, with the recovery of all valuable components, becomes of considerable importance.

2. While the raw materials have a complex composition, industry sets very high requirements with respect to the purity of the metals. In the finished product, the maximum permissible concentrations of impurities are often of the order of a few hundredths, a few thousandths, and sometimes a few ten-thousandths of one percent. In some cases the task becomes more difficult because of the need to separate elements with very similar properties (e.g., hafnium from zirconium, niobium from tantalum, isolation of individual lanthanides in a pure state).

As a result, the separation of impurities and the production of high-purity compounds plays an important part in technological processing of the raw materials.

3. None of the rare metals can be smelted directly from the ore. The ore concentrate must first be converted to pure chemical compounds which are used as the raw material for the production of the metal. The

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processing of the ore concentrate usually includes three main stages:

a) decomposition of the concentrate;
b) preparation of pure chemical compounds (oxides, salts);
c) production of the metal from the chemical compound.

The object of the first stage is to decompose the mineral, to separate the extracted metal from the bulk of the accompanying elements, and to concentrate it in solution or in the precipitate. This is accomplished either by pyrometallurgical processes (roasting, smelting, distillation, etc.) or by hydrometallurgical methods (processing with acids, alkali solutions, etc.).

The second stage consists of the isolation and purification of chemical compounds and is characterized by the major part played by chemical processes in aqueous solutions (precipitation, crystallization, extraction, ion exchange, etc.). Pyrometallurgical processes (distillation of chlorides or oxides, fractionation) are occasionally used for the production of pure compounds.

The third stage — preparation of pure rare metals — makes use of various (mainly pyrometallurgical) processes for the reduction of the chemical compounds. In accordance with the reduction methods used, rare metals may be classified into three groups (Table 6).

TABLE 6

Methods for the production of the rare metals

Method of reduction	Metal
Isolation from aqueous solutions by cementation or electrolysis	Gallium, rhenium, indium, thallium
Reduction of oxides or salts with hydrogen, carbon monoxide or carbon, at high temperatures	Tungsten, molybdenum, rhenium, germanium
Reduction of oxides or salts with metal (metallothermy) or by electrolysis in molten media	Tantalum, niobium, vanadium, titanium, zirconium, lithium, beryllium, lanthanides, thorium, uranium,

As is evident from the table, only four of the rare metals (gallium, indium, thallium and rhenium) can be isolated directly from aqueous solutions of their salts while the remaining rare metals are produced by pyrometallurgical methods.

In most cases the refractory metals are first obtained as a powder or a spongy porous mass. The metal ingots are produced from these sponges by arc or electron-beam melting in a cooled copper crucible or by powder-metallurgy techniques. The production of a number of rare metals in a pure state became possible due to the development of vacuum techniques.

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Development of the rare-metal industry in the USSR

No rare-metal industry existed in Russia before the 1917 Revolution. Nevertheless, leading Russian scientists forecast the great potentialities of various rare-metal ore deposits in the enormous area of Russia.

Important studies on the occurrence of scattered rare metals (indium, thallium, rubidium, and cesium) in Russia were conducted by V. I. Vernadskii in the years 1909—1915; they were a valuable contribution to the geochemistry of those elements. V. I. Vernadskii announced in 1916 that Russia had raw materials for the production of vanadium, lithium, lanthanum, cerium, thorium, boron, bismuth, cadmium, molybdenum, titanium, tin, radium, selenium, uranium, cesium, and zirconium. None of these metals was produced in Russia at that time.

Mendeleev's periodic table of elements played a most important part in the development of the chemistry of the rare metals. The periodic table made it possible to predict undiscovered elements and their properties and thus facilitated the prospecting work. The properties of gallium, germanium and scandium were brilliantly predicted by Mendeleev in 1871, before their discovery.

A number of new metallurgical processes which were subsequently applied to in the production of rare metals were developed by Russian scientists before the revolution. These include the powder-metallurgy (sintering) method used in the production of refractory metals (tungsten, molybdenum, tantalum, and niobium). The method was developed in 1826 by the Russian metallurgist P. G. Sobolevskii who used it in the manufacture of platinum products.

In 1860—1865 Beketov laid the scientific foundations for a very important method of metal production — thermal reduction. He discovered the aluminothermal method and was the first to use it in the production of barium, potassium, rubidium and cesium. Thermal reduction is used today in the production of many rare metals and their alloys.

Some attempts were made by Russian engineers and workers to organize small-scale production of certain rare metals and their compounds and alloys even before the Revolution. For example, molybdenum and tungsten steels were produced in 1896 in the Putilov plant under the guidance of Prof. Lipin, and their properties were investigated.

Further steps in the organization of the production of rare metals and their alloys were taken in Russia in the war years 1914—1918. During that period, a beginning was made in the small-scale exploitation of tungsten ores from the Urals and the Transbaikalia and of molybdenum ores from the Chikoi deposits, and the production of ferrotungsten was organized at the Obukhov plant in Petrograd and at the Motovilikha plant in Perm. The Izhora plant began the production of special molybdenum steels.

The production of small amounts of selenium and tellurium compounds from the wastes of sulfuric acid plants was begun in 1916. The production technology of lithium compounds from lepidolite from Russian deposits was developed under the guidance of V. G. Khlopin. At the same time, the "Elektrosila" plant in Petrograd began pilot-plant production of ferrotitanium and titanium carbide, and the conversion of the latter into titanium tetrachloride. However, these attempts were not continued.

Geological surveys of rare metals were started as early as 1922. These surveys which became very intensive during the first few five-year planning periods resulted in a sufficient supply of local raw materials being made available to the Soviet rare-metals industry.

In 1938 A. E. Fersman analyzed the surveys of raw materials in the USSR and noted that the occurrence of the following elements had not been reported: scandium, gallium, germanium, rhenium, and thallium. By now, deposits of these elements have also been discovered and investigated.

Following the successful research work of the geologists, great advances were made in mining, ore dressing, chemistry and metallurgy.

A rare-element office was set up in 1922, for the investigation and development of new technological processes for the manufacture of rare metals and their compounds. The State Institute of Rare Metals was founded in 1931. In the same year the first chairs of technology and metallurgy of rare metals were created in higher schools of engineering in the Soviet Union.

There was a rapid development in the production of rare metals in the USSR. Production of the following metals was organized: tungsten in 1927, molybdenum in 1928, hard alloys in 1929, alloys of iron with tungsten and molybdenum in 1931, beryllium in 1932, tantalum and lithium in 1933, and ferrovanadium in 1932—1935.

A very rapid development in the production of rare metals has taken place in the last 15 years (the postwar period). This was caused by the need for materials with very different physicochemical properties in modern industries: high-speed and high-flying aircraft production, electro-vacuum technology, semiconductor electronics, and production of atomic power. Thus, the need of aviation for light and refractory alloys led to the large-scale production of titanium —a metal which was a laboratory curiosity only 15 years ago. The production of germanium was organized as a result of the rapid development of semiconductor electronics. The birth of nuclear power industry necessitated the production of uranium and thorium —the

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main nuclear fuels, as well as of other nuclear reactor materials, especially zirconium, beryllium, and lithium. The rare metals are of primary importance for the further increase in the production of special steels and of ultrahard, refractory and corrosion-resistant materials, electrical illumination lamps, radio valves, X-ray apparatus, radar sets, photoelectric devices, and various parts for cars, tractors, etc.

At present, the Soviet Union produces on an industrial scale all technologically important rare metals. A continuously increasing consumption of the rare metals is due to the rapid development of the production of special steels, hard and refractory alloys, of the electrical and electronic industries and other branches of technology. As a result, it is planned to increase the production of rare metals in order to satisfy the requirements of the national economy.

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Part One

REFRACTORY METALS

Chapter I

TUNGSTEN

1. GENERAL DATA ON TUNGSTEN

Brief historical note

The element tungsten was discovered in 1781 by the Swedish chemist K. V. Scheele during the decomposition of a tungsten mineral ("heavy stone", subsequently known as scheelite) with acids. Two years later, i.e., in 1783, tungstic acid was isolated from another tungsten mineral — wolframite. In the same year, powdered tungsten was produced for the first time by reducing tungsten trioxide with carbon.

Tungsten became an important technological metal only about one hundred years after its discovery. The effect of tungsten on the properties of steel was observed in the 1850's, but tungsten steels found wide use only at the end of the nineteenth and the beginning of the twentieth centuries.

The invention of fast-cutting steels (demonstrated for the first time at the International Exposition of 1900) led to rapid technological advances which increased the efficieny of metalworking by cutting. Tungsten became one of the most important alloying metals. This was the start of the rapid development of tungsten production.

The use of tungsten in tungsten filaments of incandescent electrical lamps was first proposed and implemented by the Russian inventor A. N. Ladygin in 1900. Such use of tungsten and its subsequent use in electronics became possible only after the development of a commercial method for the production of ductile tungsten by Coolidge, in 1909.

Sintered hard alloys of tungsten carbide were developed in 1927—1928. These alloys, whose efficiency surpasses that of the best tool alloys, play an important role in modern technology.

Properties of tungsten

Tungsten belongs to Group VI of the periodic table. The appearance of massive tungsten resembles that of steel.

The melting point of tungsten is higher than the melting point of any other element except carbon. The metal is characterized by a high boiling point, a low vaporization rate at high temperatures, and a low coefficient of thermal expansion. The electrical resistivity of tungsten is about three times that of copper.

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The mechanical properties of tungsten depend to a great extent on its mechanical and thermal history. Tungsten cannot be worked mechanically in the cold; its forging, rolling, and drawing are carried out when hot.

The physical and mechanical properties of tungsten are shown below.

Atomic number	74
Atomic weight	183.92
Density, g/cm^3	19.3
Crystalline lattice type and parameter	body-centered cube $a = 3.1647$ Å
Melting point, °C	3395 ± 15
Boiling point, °C	5930
Heat of fusion, cal/g	61
Heat of vaporization, cal/g	1183
Heat capacity, cal/g.°C at:	
18°	0.031
1000°	0.0365
1400°	0.043
2100°	0.048
Thermal conductivity, cal/cm.sec °C, at:	
20°	0.31
827°	0.28
1727°	0.24
Linear expansion coefficient (0 to 500°) of forged rods	4.98×10^{-6}
Electrical resistivity ohm.cm·10^6 at:	
20°	5.5
300°	27.14
1200°	40.0
2000°	66.0
2430°	81.1
3030°	103.3
Electron work function, eV	4.55
Energy radiated by the surface, watt/cm^2, at:	
800°	0.9
1600°	18.0
2200°	64.0
2700°	153.0
3030°	255.0
Thermal neutron capture cross section, barn*	19.2
Brinell hardness, kg/mm^2:	
of a sintered rod	200 - 230
of a forged rod	350 - 400
Tensile strength, kg/mm^2:	
of a sintered rod	13
of a forged rod	35 - 150
of a nonannealed wire	180 - 415
of an annealed wire	110
Young's modulus (of a wire), kg/mm^2	35000 - 38000

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* One barn = 10^{-24} cm^2.

Tungsten is stable in air. Noticeable oxidation starts between 400 and 500° (an irridescence appearing on the surface), and vigorous oxidation to the yellow trioxide takes place at higher temperatures.

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Tungsten at temperatures below its melting point does not react with hydrogen. Reaction between tungsten and nitrogen, with formation of tungsten nitride WN_2, takes place only above 2000°.

Tungsten is rapidly oxidized by water vapor at red heat (600 to 700°) with formation of WO_3:

$$W + 3H_2O \rightleftarrows WO_3 + 3H_2.$$

Solid carbon and carbon-containing gases (CO, CH_4, C_2H_2, etc.) react with tungsten at 800 to 1000° with formation of tungsten carbides (WC and W_2C). The presence of even small amounts of carbide in the metal makes it brittle and strongly reduces its electrical conductivity.

At ambient temperatures, tungsten is not attacked by hydrochloric, sulfuric, nitric, and hydrofluoric acids at any concentration, or by aqua regia. At 80 to 100° the metal is not attacked by hydrofluoric acid; it is attacked very slowly by hydrochloric and sulfuric acids, and more noticeably so by nitric acid and aqua regia. Tungsten dissolves rapidly in a mixture of hydrofluoric and nitric acids.

Tungsten is not affected by alkali solutions at room temperature, but is oxidized by molten alkalies (in the presence of air) with the formation of tungstates. This process is very rapid in the presence of oxidizing agents ($NaNO_3$, $NaNO_2$, $KClO_3$, PbO_2).

The properties of tungsten compounds

Oxides. There are four known oxides in the W—O system. They are tungsten trioxide (or tungstic anhydride) WO_3, the dioxide WO_2, and the *intermediate oxides* W_4O_{11} *(or* $WO_{2.75}$*) and* $W_{10}O_{29}$ *(or* $WO_{2.90}$*). The composition* of the tungsten oxides may vary over a fixed range without change in crystalline structure. Thus, the composition of tungstic anhydride varies over the range $WO_{2.95-3.0}$. The composition ranges of the intermediate oxides are represented by the formulas $WO_{2.80-2.90}$ and $WO_{2.70-2.75}$ and that of the dioxide by $WO_{2.0-2.05}$.

Tungsten trioxide WO_3 is a yellow crystalline powder. Its density is from 7.2 to 7.4 [g/cm_3]. Its melting point is about 1470°. Its boiling point lies between 1700 and 2000°. The heat of formation of WO_3 is 202.8 kcal/mole.

Tungstic anhydride is sparingly soluble in water and in common inorganic acids (except hydrofluoric). Its solubility in water is 0.02 g/l.

Tungstic anhydride dissolves in solutions of alkali hydroxides and sodium carbonate, with formation of tungstic acid salts (tungstates):

$$WO_3 + 2NaOH = Na_2WO_4 + H_2O.$$

Tungsten trioxide dissolves slowly in ammonia solutions, especially if it has been ignited to a high temperature.

At 800 to 900° WO_3 may be reduced to the metallic state by both hydrogen and carbon monoxide.

Tungsten dioxide WO_2 is a chocolate-brown powder. Its density is between 10.9 and 11.1 [g/cm^3]. Its melting point is ~ 1270° and it begins to sublime at 1000°. The boiling point is ~ 1700°. The heat of formation of WO_2 is 134.0 kcal/mole.

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Tungsten dioxide is formed in the reduction of WO_3 with hydrogen at 575 to 600°.

The dioxide is insoluble in water, alkali solutions, hydrochloric acid and dilute sulfuric acid. It is oxidized by nitric acid to the higher oxide.

The intermediate oxides — $W_{10}O_{29}$ and W_4O_{11} are formed in the reduction of WO_3 with hydrogen at 300 to 550°. They may also be prepared by ignition of a mixture of tungsten and WO_3 (or of WO_3 and WO_2) in an inert atmosphere such as nitrogen.

$W_{10}O_{29}$ is a blue powder while W_4O_{11} has a violet color. The density of $W_{10}O_{29}$ is 7.1 to 7.2 while that of W_4O_{11} is somewhat higher, 7.7 to 8.0 [g/cm^3]. The heats of formation of the oxides are 193.1 and 180.3 to 163.1 kcal/mole respectively.

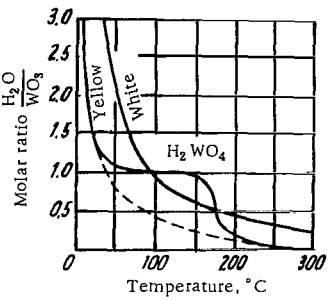

FIGURE 1. Dehydration curves of tungstic acid.

The intermediate oxides are sparingly soluble in water, in inorganic acids and in dilute alkali solutions.

Tungstic acid. Tungstic acid exists in two forms: the yellow acid which is precipitated by acids from hot tungstate solutions, and the white colloidal form which is precipitated in the cold. The yellow acid has the composition H_2WO_4. The white form is, apparently, hydrated tungsten trioxide since its dehydration curve has no breaks or plateaus (Figure 1). Water is detached from H_2WO_4 at above 188°, with the formation of WO_3. The white acid is converted into the yellow form by prolonged boiling. Tungstic acid is dissolved in solutions of alkali hydroxides, sodium carbonate and ammonia with formation of tungstates.

Tungstic acid is capable of adding various numbers of WO_3 molecules. This leads to the formation of polyacids whose composition corresponds to the general formula $xH_2O\ yWO_3 \cdot nH_2O$ where $y > x$. These acids have not been isolated in the free state (except for the metatungstic acid $H_2W_4O_{13} \cdot 9H_2O$), but their salts are known to exist. These salts are known as polytungstates. The general formula of the polytungstates is $xMe_2O \cdot yWO_3 \cdot nH_2O$. When $x = y = 1$, the salt corresponds to the normal tungstate, but polytungstates are formed when $y : x > 1$. The following types of polytungstates are known:

$Me_2O \cdot 2WO_3$ — ditungstates;

$3Me_2O \cdot 7WO_3$, $5Me_2O \cdot 12WO_3$ — paratungstates;

$Me_2O \cdot 3WO_3$ — tritungstates;

$Me_2O \cdot 4WO_3$ — metatungstates.

Unlike tungstic acid, the metatungstic acid $H_2W_4O_{13} \cdot 9H_2O$ is quite soluble in water and so are most of its salts including the calcium, iron, and copper salts, etc. The density of metatungstic acid is 3.93 [g/cm^3].

The more important tungstates. The normal sodium tungstate Na_2WO_4 is one of the technically important salts of tungstic acid. This salt is formed when WO_3 is dissolved in solutions of alkali hydroxides or sodium carbonate.

The salt crystallizes as dihydrate from aqueous solutions at above +6°; the decahydrate is stable at lower temperatures. The melting point of anhydrous Na_2WO_4 is 200°, its density is 4.18 [g/cm$_3$].

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The solubility of sodium tungstate in water is:

Temperature, °C	-5	0	5	6	10	20	40	80	100
Solubility of the anhydrous salt, %	30.6	35.4	41.0	41.8	41.9	42.2	43.8	47.4	49.2
	$Na_2WO_4 \cdot 10H_2O$			$Na_2WO_4 \cdot 2H_2O$					

Sodium paratungstate $5Na_2O \cdot 12WO_3 \cdot nH_2O$ crystallizes from solutions of normal tungstates as a result of careful neutralization to a pH of 5.5 to 6. This is accompanied by hydrolysis:

$$12Na_2WO_4 + 7H_2O \rightarrow 5Na_2O \cdot 12WO_3 + 14NaOH.$$

The alkali hydroxide formed in the reaction is neutralized by the acid.

The salt hydrates contain 28 and 25 water molecules after crystallization in the cold and at 60 to 80° respectively.

The solubility of the paratungstate in water is strongly affected by the temperature:

Temperature, °C	12.4	39.6	101.8
Solubility of the anhydrous salt, %	5.52	17.94	70 6

The melting point of the anhydrous salt is 705.8° and its density is 5.49 [g/cm^3].

Sodium metatungstate is formed by neutralizing a solution of sodium tungstate with acid to pH $\approx$ 4. When its solution is boiled for a prolonged time in the presence of an alkali, the metatungstate is converted into the normal salt.

The possibility of formation of metatungstates must be taken into account in production processes, since the presence of metatungstates in the solution may lead to incomplete precipitation of the tungstic acid.

Ammonium paratungstate $5(NH_4)_2O \cdot 12WO_3 \cdot nH_2O$ may be prepared by neutralization or evaporation of a solution of the normal ammonium tungstate $(NH_4)_2WO_4$*:

$$12(NH_4)_2WO_4 \rightarrow 5(NH_4)_2O \cdot 12WO_3 + 14NH_3 + 7H_2O.$$

Needle-shaped crystals containing 11 molecules of water are precipitated from cold solutions (below 50°); the lamellar modification containing 5 water molecules is precipitated from heated solutions. The salt is sparingly soluble in water.

The solubility of ammonium paratungstate is strongly affected by the temperature:

Temperature, °C	17	29	45	49	52	70
Solubility of the anhydrous salt, %	1.064	2.014	3.467	4.341	3.280	7.971
	$n = 11H_2O$				$n = 5H_2O$	

Calcium tungstate $CaWO_4$ is a white, fine crystalline powder which is sparingly soluble in water and whose solubility decreases with increasing temperature: from 0.0064 g/l at 15° to 0.0012 g/l at 100°. Its density is 5.98 [g/cm^3].

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* The normal ammonium tungstate exists only in aqueous solutions.

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Calcium tungstate may be prepared by precipitation on the addition of calcium chloride or lime to solutions of the alkali tungstate, or by direct solid-state interaction of calcium oxide with tungstic anhydride at 600 to 800°. Calcium tungstate is decomposed by acids, with formation of tungstic acid.

Heteropolyacids and their salts. Tungsten has a number of known heteropolyacids which form salts with phosphoric, arsenic, silicic and other acids. Those acids are formed through the substitution of $(WO_4)^{2-}$ and $(W_2O_7)^{2-}$ ions for oxygen ions in silicic, phosphoric, arsenic and other acids.

For instance, there are potassium and sodium salts of silicotungstic acid $H_8[Si(W_2O_7)_6]\cdot xH_2O$, an acid which does not exist in the free state. The composition of the potassium salt is $K_8[Si(W_2O_7)_6]\cdot xH_2O$ (where x is 12 or 20) and of the sodium salt — $Na_4\cdot H_4[Si(W_2O_7)_6]\cdot xH_2O$ (where x is 10 or 18). Salts which are derivatives of phosphotungstic or arsenotungstic acids ($H_7[R(W_2O_7)_6]$ where R = P or As) are also known to exist.

The heteropolycompounds are formed on the acidification of sodium tungstate solutions containing salts of silicic, arsenic or phosphoric acids.

Tungsten bronzes. A peculiar type of compound, known as tungsten bronzes, is formed on the reduction of sodium, potassium or lithium tungstates with hydrogen or other reducing agents, during the electrolysis of melts of these salts, or on the fusion of normal tungstates with WO_3 in the absence of air. Those bronzes have a pleasant metallic luster, metallic-type conductivity (electrical) and considerable corrosion resistance.

The composition of these tungsten bronzes corresponds to the formula $Me_2O\cdot WO_2\cdot nWO_3$ where n ranges from 1 to 4. The color of the compounds is gold-yellow where n = 1, red where n = 2, violet where n = 3 and blue where n = 4.

It is now thought that sodium-tungsten bronzes are interstitial solid solutions of sodium in WO_3. A fraction of the tungsten atoms, which corresponds to the fraction of sodium atoms filling the vacant sites in the WO_3 lattice, is converted from the hexavalent to the pentavalent state. A compound —$NaWO_3$ — is formed when all vacant sites in the lattice are filled.

Tungsten chlorides. Tungsten forms a series of chlorides: WCl_6, WCl_5, WCl_4, WCl_2, and oxychlorides: $WOCl_4$ and WO_2Cl_2.

The hexachloride WCl_6 is formed when a stream of dry chlorine is passed over tungsten powder at 750 to 800° as dark-violet crystals. The hexachloride melts at 272 and boils at 337°. It exists in two crystalline modifications: α- WCl_6 and β- WCl_6. The transition from the α- to the β-modification occurs at about 230° and is accompanied by a large change in volume.

The hexachloride is decomposed by water, with the formation of tunstic acid:

$$WCl_6 + 4H_2O = H_2WO_4 + 6HCl.$$

The tunsten oxychlorides WO_2Cl_2 and $WOCl_4$ are formed as a result of the action of chlorine on tungstic anhydride or on a mixture of WO_3 and carbon. WO_2Cl_2 is pale yellow and melts at 266°; $WOCl_4$ is red-brown, melts at 209 and boils at 232°.

The lower tungsten chlorides are formed by the reduction or thermal dissociation of the higher chlorides. The pentachloride WCl_5 is a black crystalline substance which melts at 248 and boils at 276°; WCl_4 is a gray-brown nonvolatile substance.

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Tungsten sulfides. Tungsten forms two sulfides: WS_2 which occurs in nature as the mineral tungstenite, and WS_3. The disulfide may be prepared by the interaction of sulfur vapor with powdered tungsten or WO_3 at 800 to 900°. Its structure and properties resemble those of molybdenum disulfide (see p. 105).

The trisulfide WS_3 is formed by bubbling hydrogen sulfide through hot acidified solutions of tungstates. WS_3 dissolves in alkali sulfides with formation of sulfur-containing salts. The dark-brown tungsten trisulfide is precipitated when a solution of the sulfur-containing salt is acidified:

$$Na_2WS_4 + H_2SO_4 = WS_3 + Na_2SO_4 + H_2S.$$

Tungsten carbides. Tungsten forms two carbides: WC and W_2C. Those carbides are hard, refractory substances. The melting points of W_2C and WC are 2750 and 2900° respectively. The microhardness of WC is 1760 kg/mm^2. The most common method for the production of the carbides is ignition of a mixture of powdered tungsten and carbon (carbon black) at 1000 to 1500°.

Uses of tungsten

Tungsten is widely used in modern technology both in the pure form and in alloys, the most important of which are alloy steels, hard alloys based on tungsten carbide, and wear-resistant and refractory alloys. Tungsten compounds are used in various branches of technology.

Tungsten in steels. More than half of the total amount of tungsten concentrates is used in the production of special steels.

The most important of those steels are the high-speed steels, containing 8—20% W, 2—7% Cr, 0—2.5% V, 1—5% Co, 0.5—1% C. The high-speed steels are characterized by their capacity for self-hardening in air and by the fact that their secondary hardening takes place at a high temperature (700 to 800°). As a result they maintain their high hardness and wear resistance up to 600 to 650°. For the sake of comparison, it should be noted that the tempering of high-carbon tool steels takes place at 200 to 250°. These properties, which are due to the presence of tungsten and chromium, have permitted an increase in cutting speed during mechanical working of steels from a few meters per minute to several dozens of meters. A great increase in productivity has resulted.

In addition to the high-speed steels, other tungsten and chromium-tungsten steels have also found wide use. Different brands of Cr—W steels containing 1 to 6% W and 0.4 to 2% Cr are used for the fabrication of tools: saws, cutters, dies, pneumatic tool parts, etc.

Tungsten is used as a component of magnetic steels. There are tungsten and tungsten-cobalt magnetic steels. The first of those contain 5 to 6% W and 0.6 to 0.75% C; by comparison with nonalloyed magnetic steels, they have a higher intensity of magnetization and coercive force. Even stronger magnetic properties are possessed by tungsten-cobalt steels containing 5 to 9% W and 30 to 40% Co. These steels are characterized by their very high coercive force (200 to 250 oersted).

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Hard alloys based on tungsten carbide. Tungsten carbide WC possesses very high hardness and wear resistance and is highly refractory. It has been used as the basis of the most productive hard tool alloys. These alloys contain 85 to 95% WC and 5 to 15% Co. The Co serves as a cementing component which imparts necessary strength to the alloy. Some types of alloys, used mainly in the working of steel, contain titanium, tantalum, and niobium carbides as well as WC. All these alloys are produced by powder-metallurgy techniques. They maintain their high hardness and wear resistance up to 1000 to 1100°. This has permitted a great increase in cutting speeds (to 150 to 250 m/min and higher) and a noticeable increase in the productivity of cutting processes as compared with the use of cutters made of the best tool steels. Hard alloys are used for the manufacture of working parts of cutting and drilling tools, of dies for wire drawing and of other parts requiring a high wear resistance and hardness.

Cast tungsten carbides are used in addition to sintered hard alloys (which contain cementing additives such as cobalt and nickel) in cases where the alloys need not have a high strength but only a high wear resistance and hardness (i. e., for some drilling tools and dies).

Heat-resistant and wear-resistant alloys. As it is the metal with the highest melting point, tungsten is a component of many heat-resistant alloys.

The alloys of tungsten with cobalt and chromium (the so-called stellites) are among the common wear- and heat-resistant alloys of tungsten, which have been known for a long time. Their composition is: 3 to 15% W, 25 to 35% Cr, 45 to 65% Co, and 0.5 to 2.75% C. The stellites have a high hardness and a high resistance to wear, corrosion, and high temperatures. Alloys of this type are used mainly for coating (by the "surfacing" technique) machine parts subjected to rapid wear (e. g., valves of aircraft engines, working surfaces of shears for hot cutting, dies, turbine blades, excavation equipment, plowshares, etc.).

Contact alloys and alloys for radiation shielding. The tungsten-copper (10 to 40% Cu) and tungsten-silver alloys (which are prepared by sintering) combine the high electrical and thermal conductivity of copper and silver with the wear-resistance of tungsten. As a result, these alloys are very effective materials for the production of contacts in knife switches, cut-out switches, spot welding electrodes, etc.

The same group of alloys includes the W—Ni—Cu alloys (85 to 90% W, 3 to 10% Ni, 2.5% Cu) which have a high specific gravity and are used in radiation therapy for γ-ray shielding.

Pure tungsten. Tungsten is used in the form of wires, strips and various forged products in the manufacture of electric bulbs, in electronics, and in X-ray technology. Tungsten is the best material for filaments and spirals in incandescent lamps. Its high working temperature (2200 to 2500°) provides a high luminosity, while its low vaporization rate ensures long service life. Tungsten wire is used in the production of directly heated cathodes and grids for electronic transmitting tubes, cathodes for high-voltage rectifiers, and heaters for indirectly-heated cathodes in various electronic devices. Tungsten is used in the production of anticathodes and cathodes in X-ray and gaseous-discharge tubes, for the contacts in electric equipment and for the electrodes in atomic hydrogen torches. Tungsten wire and rods are used as electric heaters in high-temperature furnaces (up to 3000°). The tungsten heating elements operate in an atmosphere of hydrogen or an inert gas, or in vacuo.

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Recently, alloys of tungsten with other refractory metals (tantalum, niobium, molybdenum, rhenium) have found use as refractory materials in aircraft and rocket technology and in other branches which require machine, engine, and tool parts which are highly refractory.

Chemical compounds of tungsten. Sodium tungstate is used in the manufacture of several brands of light-fast lacquers and pigments. In addition, sodium tungstate is used in the textile industry for the weighting of tissues and as a mixture with ammonium sulfate and phosphate for the production of heat-resistant and water-repellent tissues.

Tungstic acid is used as an adsorbent, as a mordant and a pigment in the textile industry, and as a catalyst in the production of high-octane gasoline in the chemical industry.

The tungstates of lead, zinc, and barium are used as fillers for white lead. Tungsten disulfide (WS_2) is used as a catalyst in the production of synthetic gasoline.

2. MINERALS, ORES, AND ORE CONCENTRATES

Tungsten minerals

The abundance of tungsten in the Earth's crust is low. Its concentration in the Earth's crust is only 1×10^{-4}%. The metal itself is not found in nature in the native state.

There are about 15 known tungsten minerals. Most of these are tungstates — salts of tungstic acid. The only minerals of practical value are those belonging to the wolframite and scheelite groups.

Wolframite [$(Fe, Mn)WO_4$] is an isomorphous mixture (solid solution) of iron tungstate ($FeWO_4$) and manganese tungstate ($MnWO_4$). These salts have crystalline lattices of the same type, with similar lattice parameters, and thus crystallize together with Fe and Mn atoms substituted for each other in the lattice sites. Wolframite containing less than 20% manganese tungstate (i. e., when the iron tungstate is predominant) is known as ferberite, while in cases in which manganese tungstate is the main component (above 80%) it is known as hübnerite.

The mixtures between these compositions are known as wolframites. The minerals belonging to the wolframite group have a black, brown, or red-brown color and a high density, 7.1 to 7.9. Their hardness is 5 to 5.55 (Mohs scale). These minerals contain between 76.3 and 76.6% WO_3. Wolframite is slightly magnetic.

Scheelite $CaWO_4$ is nearly pure calcium tungstate. Its color may be white, yellow, gray or brown. Its density is 5.9 to 6.1 and its hardness is 4.5 to 5. Scheelite often contains some powellite $CaMoO_4$. Under ultraviolet illumination scheelite exhibits a sky-blue or blue fluorescence. The fluorscence becomes yellow if the molybdenum content is more than 1%. Scheelite is not magnetic.

Other tungsten minerals of no commercial value are: tungstite or tungsten ochre $WO_3 \cdot H_2O$, cuprotungstite $CuWO_4 \cdot H_2O$, stolzite $PbWO_4$, chillagite $3PbWO_4 \cdot PbMoO_4$, ferritungstite $Fe_2O_3 \cdot WO_3 \cdot 6H_2O$, and tungstenite WS_2.

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Tungsten ores and deposits

The tungsten ores are usually of low tungsten content. The richest ores contain 0.5 to 2.0% WO_3. In addition to the tungsten minerals, the ores contain molybdenite, cassiterite, pyrite, arsenopyrite, chalcopyrite and other minerals. Wolframite is most often associated with tin.

With respect to their mineralogical compositions, there are two types of deposits — wolframite and scheelite; they exist in two forms — vein and contact types.

The largest fraction of the tungsten minerals in vein deposits lies in quartz veins 0.3 to 1.0 m thick. The WO_3 concentration in ores of this type ranges from 0.4 to 2%. Deposits of the contact type are related to the contact zones between granite rocks and limestone. Scheelite-bearing skarn (sileceous limestone) strata are characteristic of this type. Scheelite is often accompanied by molybdenum minerals — molybdenite (MoS_2) and powellite ($CaMoO_4$). Ores of this type occur in the USSR, the USA, and Canada.

During weathering of the vein deposits, the wolframite and scheelite (which are stable minerals) accumulate with the formation of placers. In these, the wolframite is often associated with cassiterite.

The tungsten deposits form a segmented ring round the shores of the Pacific Ocean: Burma, China, Korea, the USA, Mexico, Bolivia, Argentina, and Australia.

Tungsten deposits exist and are exploited at a number of locations in the USSR — the Urals, Altai, the Caucasus, Central Asia, the Transbaikalia and the Far East.

The world production of tungsten concentrates (60% WO_3) in 1960 was about 55,000 tons (not including the USSR).

The enrichment of tungsten ores

The task of enrichment is to produce ore concentrates which are subsequently used in the smelting of ferrotungsten or are suitable for chemical or metallurgical processing. The standard concentrates contain 55 to 60% WO_3 and a limited amount of impurities (Table 7).

The degree of enrichment, i.e., the ratio of the tungsten concentration in the concentrate to that in the ore, ranges (depending on the tungsten content of the ore) from 30 to 120.

The tungsten ores are enriched by different methods: gravitation, flotation, magnetic and electrostatic separation, and chemical enrichment methods.

The sky-blue fluorescence of scheelite under ultraviolet light is used for preliminary ore sorting in dark rooms.

Because of their high densities, wolframite (7.1 to 7.9) and scheelite (5.9 to 6.1) can be separated from quartz (2.6) and other low-density minerals by wet jigging and concentration on tables and sluices. However, the gravitation method does not ensure the separation of cassiterite (density = 6.8 to 7) and sulfide minerals from wolframite and scheelite.

In the case of minerals containing embedded particles of coarse grain structure, the separation of wolframite from cassiterite can be

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successfully achieved by electromagnetic separation in a high-intensity magnetic field (wolframite is slightly magnetic while cassiterite is non-magnetic). The magnetic separation is occasionally preceded by calcination, which converts the pyrite into the magnetic oxide Fe_3O_4 this being subsequently separated from the wolframite in a low-intensity magnetic field.

TABLE 7

Technological requirements for some types of tungsten concentrates (GOST 213-56)

Concentrate brand	Type of concentrate	Chemical composition,%								Use
		tungsten trioxide (minimum)	impurities (maximum)							
			SiO_2	P	S	As	Sn	Cu	Mo	
KVG	Wolframite-hübnerite	65	10	0.04	0.5	0.2	0.2	0.2	—	Production of ferrotungsten
KVGT	Wolframite-hübnerite	60	5	0.10	0.8	0.10	1.00	0.15	0.06	Production of hard alloys and tungsten metal
$KShT_1$	Scheelite	55	—	0.20	0.8	0.10	0.20	0.20	0.04	
$KShT_2$	"	55	—	0.20	0.8	0.10	0.20	0.20	0.30	

The magnetic separation of wolframite from cassiterite is hindered when the cassiterite is coated with an iron oxide layer. In such a case the iron oxide is dissolved in advance by treating the wolframite-cassiterite concentrates with hot solutions of sulfuric or hydrochloric acids.

Unlike wolframite, scheelite is non-magnetic and cannot be separated from cassiterite by magnetic separation. Scheelite is separated from cassiterite by flotation or by electrostatic separation, which is based on differences in the electrical conductivity of the minerals. Chemical separation methods are used occasionally.

Gravitation methods provide a satisfactory means for the isolation of tungsten from wolframite ores and up to now are the main way in which these ores are enriched. When scheelite ores are enriched by gravitation methods, the extraction of tungsten does not exceed 70%, because of the tendency of scheelite towards overdisintegration. This leads to the formation of fines and to considerable losses of tungsten in the tailings.

Recently, flotation methods have become the main means of enriching scheelite ores, especially if they are lean and finely impregnated. During flotation, sodium carbonate, water glass and tannin are used as depressors and pH-control agents; oleic acid, sodium oleate, and liquid soap are used as collectors; and pine oil, terpinol, technical grade cresol and other reagents are used as frothing agents. The flotation is carried out in an alkaline medium at a pH of 9 to 10. The addition of copper and iron sulfates to the water glass assists the depression of calcite, fluorite and apatite.

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A combined method, involving flotation and gravitation together with chemical treatment, is used occasionally for enriching scheelite ores.

In many cases the powellite ($CaMoO_4$) present in scheelite-type ores can be separated only if it is not bound isomorphously to the scheelite. As a result, scheelite concentrates often contain molybdenum, which is separated during the hydrometallurgical processing of the concentrates.

The concentrations of various impurities are adjusted to the predetermined limits by various chemical processes. Thus, the phosphorus content of scheelite is reduced by treating it in the cold with hydrochloric acid. Calcite and dolomite are removed at the same time. To separate copper, arsenic, and bismuth the concentrates are first calcined and then treated with acid or processed by other methods. The adjustment of the impurity content to a predetermined level is especially important in the case of concentrates used for smelting of ferrotungsten. Concentrates with greater impurity content may be used occasionally in hydrometallurgical processing.

3. PROCESSING OF TUNGSTEN CONCENTRATES

The main product formed in the direct processing of tungsten concentrates (in addition to ferrotungsten for ferrous metallurgy) is tungsten trioxide. It is used as the starting material for the production of tungsten and tungsten carbide — the main component of hard alloys.

There are several industrial processing methods of the concentrates. The selection of the method to be used depends on the type of raw material (wolframite or scheelite concentrate), the production volume, the requirements with respect to the purity of the tungsten trioxide and its physical properties (particle size of the powder) and a number of conditions which determine the cost of processing. Each kind of scheme for the processing of tungsten concentrates comprises the following stages:

1) decomposition of the concentrate;
2) production of technical grade tungstic acid;
3) purification of the technical grade acid and manufacture of the required commercial product.

The processing techniques of wolframite and scheelite concentrates differ mainly in their decomposition stage. The subsequent operations involving the separation of tungstic acid and its purification are similar.

The following methods for the decomposition of tungsten concentrates are used in industry.

The wolframite and scheelite concentrates are calcined or fused with sodium carbonate, and the product is leached with water or treated in an autoclave with an aqueous solution of sodium carbonate. Wolframite concentrates are occasionally treated with an aqueous solution of sodium hydroxide. Scheelite concentrates are decomposed with acids.

Aqueous solutions of sodium tungstate are obtained whenever alkaline reagents (sodium carbonate, sodium hydroxide) are used for the decomposition; tungstic acid or some other tungsten compound is then precipitated from such solutions.

When acids are used for the decomposition of the concentrates, the product is a precipitate of technical grade tungstic acid contaminated with impurities. It is purified in subsequent operations.

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The individual techniques used in the processing of wolframite and scheelite concentrates are described below. Technological operations common to both types of concentrates (e. g., treatment of sodium tungstate solutions) are described in detail only in the section dealing with the production of tungsten trioxide from wolframite.

4. DECOMPOSITION OF WOLFRAMITE CONCENTRATES

Fusion with sodium carbonate /1—3/

This is the most common commercial method for the decomposition of wolframite. A technical flow sheet for the processing of wolframite concentrates by this method is shown in Figure 2.

Fusion. The interaction of wolframite with sodium carbonate in the presence of oxygen may be described as follows:

$$2FeWO_4 + 2Na_2CO_3 + {}^1/_2O_2 \rightarrow 2Na_2WO_4 + Fe_2O_3 + 2CO_2,$$
$$3MnWO_4 + 3Na_2CO_3 + {}^1/_2O_2 \rightarrow 3Na_2WO_4 + Mn_3O_4 + 3CO_2.$$

The reactions are virtually irreversible since the CO_2 is removed from the reaction zone.

The reaction takes place at 800 to 900°. A 10 to 15% excess of sodium carbonate above the stoichiometric amount required ensures a nearly quantitative (98 to 99.5%) decomposition of the concentrate. An oxidant (saltpeter, in an amount corresponding to 1 to 4% by weight of the concentrate taken) is occasionally added in order to accelerate the oxidation of iron.

During fusion with sodium carbonate, the common impurities in the wolframite concentrate (silicon, phosphorus, arsenic, molybdenum, and other compounds) form soluble sodium salts:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2;$$
$$Ca_3(PO_4)_2 + 3Na_2CO_3 = Na_3PO_4 + 3CaCO_3;$$
$$As_2S_3 + 6Na_2CO_3 + 7O_2 = 2Na_3AsO_4 + 3Na_2SO_4 + 6CO_2;$$
$$MoS_2 + 3Na_2CO_3 + 4{}^1/_2O_2 = Na_2MoO_4 + 2Na_2SO_4 + 3CO_2.$$

The tin-containing mineral cassiterite (SnO_2) does not react with sodium carbonate to any significant extent. There is virtually no formation of sodium stannate. The excess sodium carbonate reacts with the iron oxide, yielding sodium ferrite:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2.$$

When the fused mass is leached with water, the ferrite decomposes with formation of sodium hydroxide:

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3.$$

Depending on the temperature, the reaction mixture at 800 to 950° is either a semi-fused dough-like cake or a liquid.

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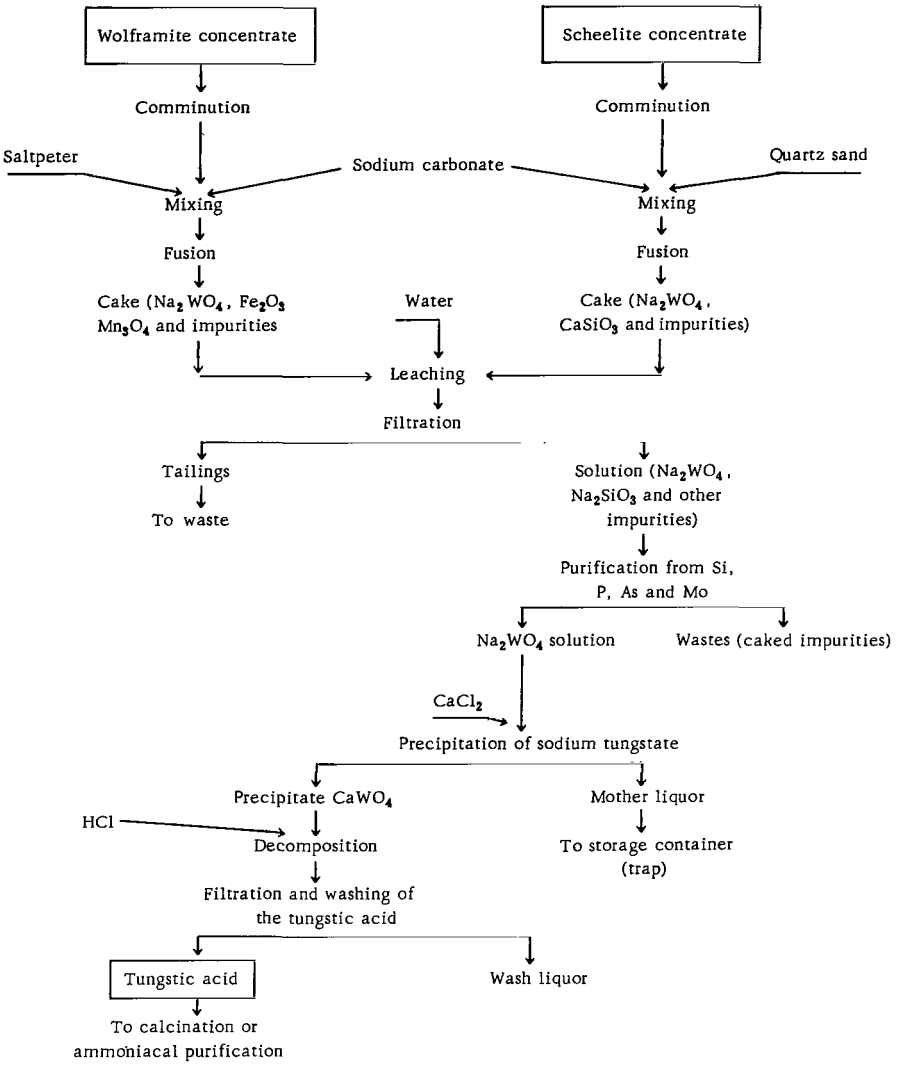

FIGURE 2. Processing of tungsten concentrates by fusion with sodium carbonate.

The cake contains sodium tungstate, iron (as the oxides and ferrite), manganese oxides, sodium salts of the impurities, excess sodium carbonate, and unreacted wolframite.

In industrial processing, the fusion of the wolframite concentrate is carried out in batch or continuous-operation furnaces. The batch process is to be preferred in small-scale production. The charge is then fused in small reverberatory furnaces with a base area of about 6 to 8 m^2.

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Continuous processes are preferably used for large-scale production. Tubular rotating furnaces lined with chamotte bricks are employed in the continuous process.

In a method developed in the USSR (by Bogomol'skaya, Semenovykh, Matusevich, et al.), the composition of the charge is designed for it not to melt but to remain in the form of particles that can be caked /3/. This protects the lining from corrosion by the melt and prevents deposit formation in various parts of the furnace. In order to prevent melting of the charge the solid tailings from the leaching of the cake are added to it in an amount calculated to reduce the WO_3 content to about 20 to 22%.

The extent of decomposition of the concentrate in this case is fairly high — 98 to 99%. The disadvantage of the process lies in the fact that the concentrates are diluted with the tailings, which leads to a decrease in the output of the furnace. However, this disadvantage is offset by the fact that standard rotating furances can be used and by the long service life of the furnace.

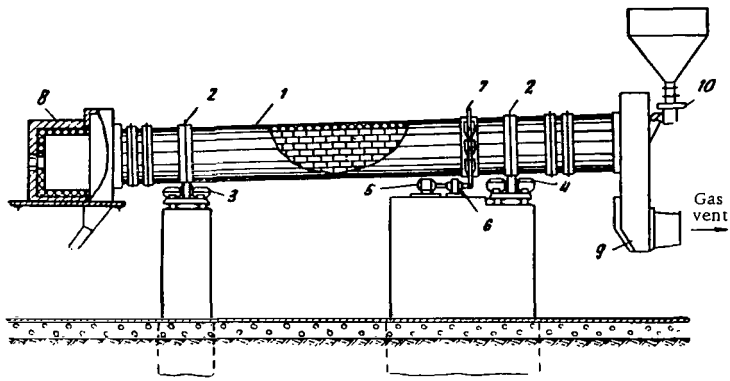

FIGURE 3. Tubular rotating furnace.

1—furnace drum; 2—supporting bands; 3, 4—supporting rollers; 5—electric motor; 6—reduction gear; 7—drive gear; 8—combustion chamber; 9—gas-venting chamber; 10—feeder.

The rotating furnaces employed (Figure 3) are 20 to 25% meters long, lined with wedge-shaped chamotte bricks. The internal diameter of the furnace is about 1.8 to 2.0 m. The rotating drum lies on rollers and is inclined some 2 to 3° towards the discharge end of the furnace. The upper and lower ends of the drum are accommodated in furnace heads. The furnace head is a chamber lined on the inside with refractory brick. The lower (combustion) chamber is fitted with a chute to discharge the material from the furnace. The upper (gas-venting) chamber has a device for feeding the charge into the furnace (charging pipe or conveyor) and is connected through the gas-venting system with an exhaust fan which creates a draft in the furnace. The drum is separated from the feed chamber by a seal which prevents leakage of air into the furnace. Occasionally, the furnace heads are detachable. The furnace is heated with powdered fuel (coal dust), fuel oil, or producer gas, supplied through burners or jets

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located in the lower furnace head. The temperature is controlled by adjusting the rate of supply of the fuel or air to the burner or jet. The furnaces are rotated at 0.5 to 2 rpm.

A furnace 20 m long and with an external diameter of 2.2 m rotating at a speed of 2.5 rpm and placed at a slope angle of 3°, has an output of 25 tons/day (for a charge containing 20 to 22% WO_3).

When a rotating furnace is used the charge must be fed in continously. The comminution of the concentrate is usually carried out in ball mills with a peripheral discharge (through screening cloths), which operate in a closed cycle with an air separator.

The charge components (concentrate, soda, and saltpeter) are fed from the storage bins to the mixer-conveyor with the aid of dosing devices (automatic balance) and a conveyor system. When prepared, the charge is fed into the hopper of the furnace. At the exit of the furnace, the fused particles are passed through a roller crusher (the crushed particle size is 2 to 5 cm) into a continuous wet mill and the resulting pulp is fed into a leaching apparatus fitted with a stirrer (Figure 5).

Leaching. The following components of the cake are dissolved when it is leached with water: sodium tungstate, soluble salts of impurities such as sodium silicate Na_2SiO_3, sodium monohydrogen phosphate, and monohydrogen arsenate, Na_2HPO_4 and Na_2HAsO_4*, sodium molybdate Na_2MoO_4, sodium sulfate Na_2SO_4, and unreacted sodium carbonate. The solid residue contains the oxides and hydroxides of iron and manganese, undecomposed concentrate, and other insoluble compounds.

The leaching is carried out at 80 to 90° in batch or continuous equipment (reactors with stirrers or drum leachers) made of iron. As a rule, two- or three-stage leaching is carried out in order to ensure quantitative extraction of tungsten. Regular or superheated steam is used for heating. The use of superheated steam is less convenient, since this leads to dilution of the solution by the condensate.

In the continuous process, the leaching is carried out in rotary drum leachers; each leacher consists of a steel drum (Figure 4) with steel lids (fitted with hollow pivots fastened to the bearings) bolted to its ends. The inner part of the casing and the marginal walls of the lids are protected by removable armor plates. The drum is rotated by a motor, through a reduction gear which transmits the motion to a toothed wheel fastened on the end lids. The leacher is held in a horizontal position on two supports. In order to accelerate leaching and, at the same time, to crush the cake particles, the leaching apparatus is filled with crushing rods 40 to 80 mm in diameter. The hot fused mass is continuously charged through the hollow pivot together with hot water (or a weak solution of sodium tungstate). The pulp is continuously discharged through the second hollow pivot.

A fairly high degree of extraction of the tungsten (about 98 to 99%) is obtained during the leaching. The concentrated sodium tungstate solutions have a density of 1.26 to 1.40 (depending on the process conditions), i.e., contain 190 to 270 g WO_3 in one liter of solution. The dry residues from leaching and filtration amount to about 30 to 40% by weight of the starting concentrate (without taking into account the residues

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* In weakly alkaline solutions, most of the phosphorus and arsenic is present as the HPO_4^{2-} and $HAsO_4^{2-}$ ions rather than as the PO_4^{3-} and AsO_4^{3-} ions.

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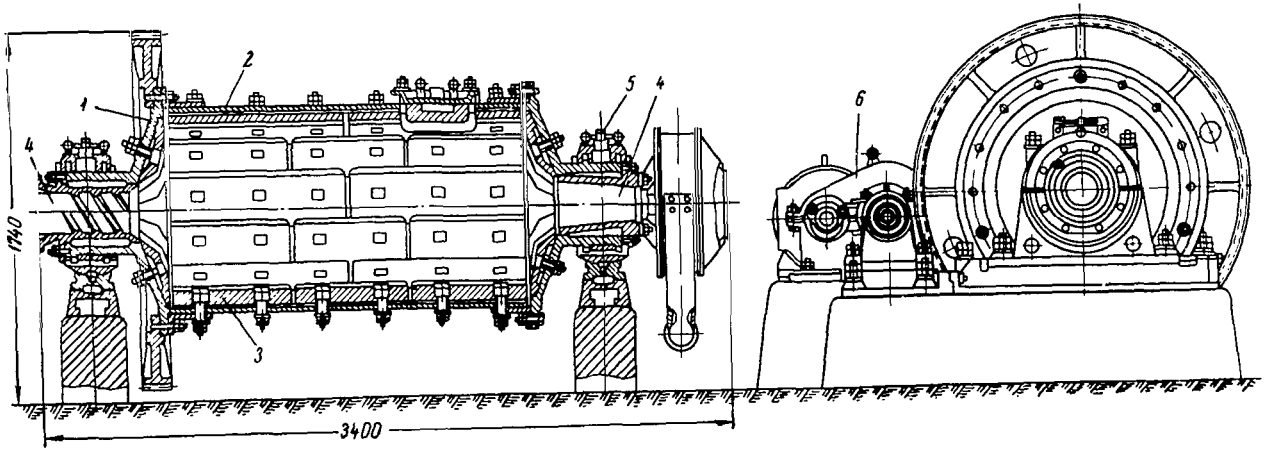

FIGURE 4. Drum-type leacher.

1—end lid; 2—steel casing; 3—armor plates; 4—hollow pivots; 5—bearings; 6—reduction gear.

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added to the charge in the continuous firing process). The WO_3 content of the tailings ranges from 1.5 to 2%. Residues containing over 2% WO_3 are recycled (to the charge-mixing stage).

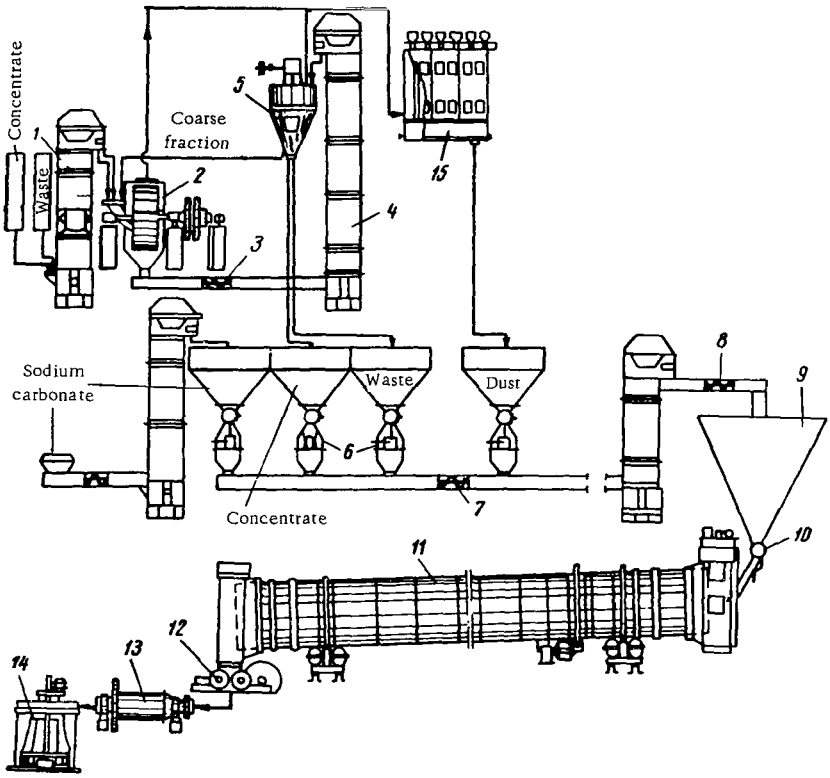

FIGURE 5. Diagram of installation for the continuous fusion and leaching process.

1—elevator; 2—ball mill; 3—conveyor (screw); 4—elevator; 5—air separator; 6—automatic dosing devices; 7—conveyor; 8—mixing conveyor; 9—charge bin; 10—feeder; 11—furnace; 12—roller crusher; 13—drum leacher; 14—reactor with stirrer; 15—filter.

In batch leaching processes, the filtration is carried out with suction filters, filter presses (with cast iron or wood frames), or other filters. Vacuum filters (disc, drum, band, etc.) are used in the continuous process. Disc filters are the most convenient to use (because of the smaller energy consumption and the easy and fast replacement of the cloths and individual filtration cells).

The equipment used for the continuous fusion and leaching process is shown in Figure 5.

Decomposition with sodium hydroxide solutions [1, 2]

A double decomposition reaction, with the formation of sodium tungstate and ferrous and manganous hydroxides, takes place when finely divided wolframite is brought into contact with a solution of sodium hydroxide.

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$$FeWO_4 + 2NaOH \rightleftarrows Na_2WO_4 + Fe(OH)_2,$$
$$MnWO_4 + 2NaOH \rightleftarrows Na_2WO_4 + Mn(OH)_2.$$

As compared with fusion with sodium carbonate, the method has the economic advantage of not requiring the use of a furnace. It has the drawback that only very finely divided concentrate may be used (i.e., investment in comminution equipment) and that it requires a large excess of sodium hydroxide, which is much more expensive than sodium carbonate. If the particle size employed is 0.03—0.04 mm, the temperature is 100—110°, and the excess of sodium hydroxide is 50% or more above the theoretical amount, a high extent of decomposition (98—99%) is obtained.

The oxidation of the ferrous and manganous hydroxides to ferric and manganic hydroxides is accelerated by bubbling air through the solution.

The decomposition is carried out in steel vats fitted with stirrers and heated with regular steam.

Soviet workers (Meerson and Nadol'skii /5/) have shown that the consumption of alkali may be reduced and the decomposition may be accelerated by conducting the alkali processing in heated ball mills. The increase in the reaction rate is attributed to the abrasive action of the balls, which remove the iron and manganese hydroxide layers from the surface of the concentrate particles.

5. PROCESSING OF SODIUM TUNGSTATE SOLUTIONS

Removal of impurities from the solutions

Sodium tungstate solutions are contaminated with silicon, phosphorus, arsenic, molybdenum, and sulfur (in the form of sodium salts) and these may cause contamination of the tungstic acid. Preliminary purification of the solutions from contaminants often leads to the production of tungstic acid of a degree of purity which permits the production of hard alloys without the need for additional purification.

Some contaminants, such as phosphorus and arsenic compounds, interfere with the sedimentation of tungstic acid. They may also cause losses of tungsten probably owing to formation of sodium heteropolytungstates (silico-, arseno- and phosphotungstates) in solution.

Removal of silicon. Preliminary purification from silicon is necessary if the SiO_2 concentration in the solution is more than 0.1% of the WO_3 concentration. The most common purification method is based on the precipitation of silicic acid in a given pH range. The process is based on the fact that sodium silicate hydrolyzes when the solution is neutralized to a pH between 8 and 9:

$$Na_2SiO_3 + H_2O \rightleftarrows H_2SiO_3 + 2NaOH.$$

When the solution is boiled, the silicic acid coagulates and separates out as a voluminous precipitate.

The lyes are usually neutralized with hydrochloric acid. The precipitation is carried out in solutions containing 130 to 150 g/l WO_3 (solution

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density 1.16 to 1.20). Hydrochloric acid is added to the sodium tungstate solution after the latter has been heated to boiling. In order to prevent localized over-acidification, (which may lead to the formation of silico- and metatungstates which reduce the degree of extraction of tungsten from the solutions in subsequent operations) the acid is added slowly, in a thin stream, with continuous stirring. The neutralization is controlled by titration of aliquots of the solution, using phenolphthalein as indicator.

Ammonium chloride, which hydrolyzes in aqueous solutions with the formation of hydrochloric acid (which neutralizes any alkali in the solution) is used occasionally as the neutralizing agent, instead of hydrochloric acid:

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl,$$
$$NaOH + HCl \rightleftarrows NaCl + H_2O.$$

The use of ammonium chloride eliminates the hazard of localized over-acidification. Moreover, the use of ammonium chloride is compatible with the subsequent removal of phosphorus and arsenic.

Removal of phosphorus and arsenic. Arsenic and phosphorus may be precipitated from the solutions as magnesium phosphate and arsenate.

The ammonia-magnesium process, based on precipitation of the sparingly soluble magnesium ammonium phosphate and arsenate ($Mg(NH_4)PO_4 \cdot 6H_2O$ and $Mg(NH_4)AsO_4 \cdot 6H_2O$) from the solution is the best purification method. The solubility of these salts in water at 20° is 0.053 and 0.038% respectively. The solubility is further reduced by the presence of Mg^{2+} and NH_4^+ ions.

The precipitation reactions may be expressed by means of the following equations:

$$Na_2HPO_4 + MgCl_2 + NH_4OH = Mg(NH_4)PO_4 + 2NaCl + H_2O,$$
$$Na_2HAsO_4 + MgCl_2 + NH_4OH = Mg(NH_4)AsO_4 + 2NaCl + H_2O.$$

The magnesium ammonium salts may hydrolyze with the formation of more soluble acid phosphates and arsenates:

$$Mg(NH_4)PO_4 + H_2O \rightleftarrows MgHPO_4 + NH_4OH.$$

As is evident from the above equation, a certain excess of ammonia must be present in solution in order to prevent hydrolysis. The presence of ammonium chloride is also necessary since it prevents precipitation of magnesium hydroxide by reducing the OH^--ion concentration to the extent where the solubility product of $Mg(OH)_2$ is not reached.

The precipitation of magnesium ammonium phosphates and arsenates is carried out in the cold. The required concentration of ammonia and ammonium chloride in the solution is established and an excess of a magnesium chloride solution is added.

At a certain reagent ratio a crystalline precipitate consisting of the magnesium ammonium salts is formed in the solution, on prolonged (up to 48 hours) standing. The gelatinous normal phosphate and arsenate ($Mg_3(PO_4)_2$ and $Mg_3(AsO_4)_2$) are partially precipitated together with the ammonium salts.

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Removal of molybdenum. Molybdenum must be eliminated from the sodium tungstate solution if its concentration exceeds 0.3 g/l*.

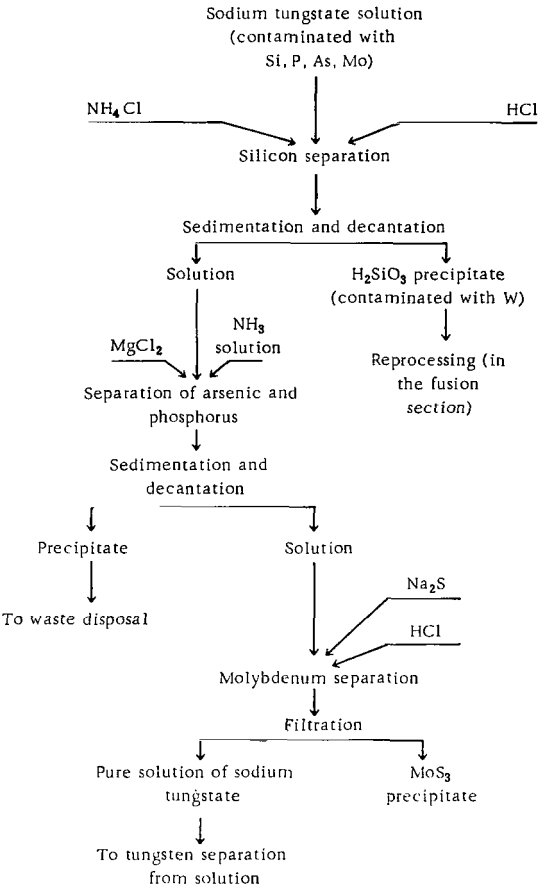

FIGURE 6. Purification of sodium tungstate solutions.

The most satisfactory commercial method for the separation of molybdenum from tungsten is based on the precipitation of molybdenum as MoS_3. Separation may be brought about by this method owing to the fact that the sulfides of molybdenum and tungsten form under different conditions. When a small amount of Na_2S (sufficient for the formation of molybdenum sulfide alone) is added to the solution, molybdenum can be precipitated quantitatively (as MoS_3) by adjusting the pH to between 2.5 and 3. The method is based on the reaction:

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* If the molybdenum concentration is lower, it may be removed during isolation of the tungstic acid and its subsequent purification.

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$$Na_2MoO_4 + 4Na_2S + 4H_2O = Na_2MoS_4 + 8NaOH,$$
$$Na_2MoS_4 + 2HCl = MoS_3 + 2NaCl + H_2S.$$

Oxysulfides, such as $MoOS_2$, are partially coprecipitated with the MoS_3, since the solution contains some oxysulfide salts (Na_2MoOS_3 and others).

Sodium sulfide is added to the solution is in accordance with the above equation. The solution is then neutralized to pH $\approx$ 3 (using Congo Red paper as the indicator). A brown precipitate consisting of molybdenum trisulfide (and oxysulfides) is formed after heating the solution for 1 to 2 hours. Not more than 1% of the tungsten present in the solution is coprecipitated with the molybdenum.

The weakly acid solution remaining after the molybdenum separation stage contains sodium metatungstates, which may cause a non-quantitative precipitation of tungsten from solution in subsequent operations. In order to decompose the meta salts, sodium hydroxide is added and the solution is boiled. The meta salts decompose in an alkaline medium. The molybdenum separation stage usually follows the arsenic and phosphorus separation stage.

The purification of sodium tungstate solutions is diagramatically shown in Figure 6. The separation of silicon, phosphorus, and arsenic from solution is carried out in iron or wooden vats fitted with stirrers, while the separation of molybdenum is carried out in iron vats coated with rubber or with some acid-resistant lining for protection against corrosion. The vats must be fitted with efficient exhausts to remove the hydrogen sulfide formed in the process.

Isolation of tungsten compounds from solution

The tungsten may be isolated from sodium tungstate solutions in the form of various compounds. Three different methods are used in practice.

1. Direct isolation as tungstic acid.
2. Precipitation of calcium tungstate and its subsequent decomposition with acids.
3. Crystallization of sodium tungstate or paratungstate.

The direct precipitation of tungstic acid would appear to be the simplest method. However, it is associated with many difficulties because of the formation of fine precipitates which tend to become colloidal. This method is occasionally used for the production of finely divided tungstic acid. The second method produces coarser precipitates of tungstic acid, which are easier to wash. This is an important advantage which explains its more common use in industry. The crystallization of sodium tungstates is used only if these salts are the required final product.

Precipitation of tungstic acid. Tungstic acid is usually precipitated from the sodium tungstate solution with the aid of hydrochloric acid:

$$Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl.$$

The nature of the resulting precipitate depends on the concentration of the starting solution, the temperature, and the method of precipitation. A colloidal precipitate of white tungstic acid is formed during precipitation from cold dilute solutions. Coarser precipitates of yellow tungstic acid,

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which may be washed with relative ease, are formed when a hot concentrated solution of sodium tungstate is poured into boiling hydrochloric acid. The rate of introduction of the solution into the hydrochloric acid affects the particle size of the precipitate. This may be due to the fact that different rates of pouring bring about formation of different numbers of crystallization centers which, at a given rate of growth of the crystals, determine the particle size of the precipitate.

The tungstic acid is precipitated in earthenware reactors or in iron reactors lined with rubber or with acid-resistant material.

A sodium tungstate solution containing 110 to 120 g WO_3/l is heated to 80 to 90° and added at a predetermined rate to a boiling 25 to 30% solution of hydrochloric acid. The rate of addition is determined empirically, depending on the required particle size of the acid. The purity and the particle size of the acid also depend on the final acidity of the solution, which is maintained in the range between 7 and 12%.

The precipitated tungstic acid must be thoroughly rinsed to remove sodium chloride and other soluble contaminants. The multiple washing is carried out first by decantation with hot distilled water and then in suction-filters which are lined with rubber or some other acid-resistant material. The washing is repeated 6 to 8 times; HCl or NH_4Cl is added to the water used in the third rinsing to a concentration of 1% in order to permit better sedimentation of the tungstic acid. Glass or chlorinated PVC cloth is used as the filter material. Further amounts of water are removed from the filtered acid by centrifuging.

The total yield at the precipitation stage is 98 to 99%, and the losses during washing amount to 0.3 to 0.4%.

Precipitation of calcium tungstate. The most widely used method for the isolation of tungsten compounds from solution is the precipitation of calcium tungstate (artificial scheelite). A fairly complete precipitation may be obtained because of the low solubility of calcium tungstate, which decreases as the temperature is increased (see p. 5). At the same time, sodium ions remain in the mother liquor, and the acid obtained has a low content of sodium-containing contaminants.

To effect the precipitation, an aqueous solution of calcium chloride is usually added to the sodium tungstate solution. A crystalline precipitate, which settles readily, is formed:

$$Na_2WO_4 + CaCl_2 = CaWO_4 + 2NaCl.$$

The completeness of the precipitation of calcium tungstate depends on the alkalinity and concentration of the sodium tungstate solution. It is recommended that the precipitation be carried out from solutions heated to boiling, and having a density of 1.14 to 1.16 (120 to 130 g WO_3/l) and an alkali hydroxide content of 0.3 to 0.7%. Incomplete precipitation is observed if the hydroxide concentration is below 0.3%, while the precipitate formed in the presence of more than 0.7% hydroxide is voluminous, settles slowly, and entrains impurities.

Other sparingly soluble calcium salts, $CaSO_4$, $CaCO_3$, $CaSiO_3$, $Ca_3(PO_4)_2$, and $CaMoO_4$, are coprecipitated with calcium tungstate. The concentrations of silicon, phosphorus, and molybdenum in the $CaWO_4$ precipitate are considerably reduced by the preliminary purification. The calcium sulfate concentration in the precipitate depends on the initial concentration of

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sulfate ions in the solution and on the excess of the calcium chloride precipitant used. The larger the excess taken, the higher the concentration of $CaSO_4$ in the precipitate. The considerable solubility of $CaSO_4$ (2g/l at 20°) permits its removal by washing with hot water.

Calcium hydroxide as slaked lime may also be used to precipitate calcium tungstate; however, the precipitate then contains more impurities.

The precipitation of calcium tungstate is carried out in iron or wooden vats fitted with stirrers.

The extent of precipitation of tungsten from solution is 99 to 99.5%. The concentration of WO_3 in the mother liquor should not exceed 0.05 to 0.07 g/l.

The washed precipitate, as a slurry or a paste, is decomposed by heating with hydrochloric acid:

$$CaWO_4 + 2HCl \rightleftarrows H_2WO_4 + CaCl_2.$$

A high final acidity of the slurry (90 to 100 g HCl/l) is maintained during the decomposition stage; this ensures that the phosphorus, arsenic and part of the molybdenum are separated from the tungstic acid precipitate (molybdenic acid dissolves in hydrochloric acid).

The acid decomposition of calcium tungstate is carried out in iron reactors lined with rubber or some other acid-resistant coating and fitted with rubber-lined mechanical stirrers.

Hydrochloric acid is heated to 60 to 65° and the aqueous slurry or paste containing the calcium tungstate is added with constant stirring. The spent acid usually contains 0.3 to 0.5 g WO_3/l, which is recovered as calcium tungstate by precipitation with lime.

The tungstic acid is washed by the method described above. The total degree of extraction is 98 to 99%. The filtered and dried acid usually contains 0.2 to 0.3% of impurities.

6. PROCESSING OF SCHEELITE CONCENTRATES

Fusion with sodium carbonate

In contrast with the fusion of wolframite concentrates, the fusion of scheelite concentrates with sodium carbonate does not ensure a satisfactory leaching of tungsten even if a large excess of sodium carbonate is added to the charge. At the fusion temperature (800 to 900°) the reaction equilibrium is shifted to the right, viz., the formation of Na_2WO_4. However, the reverse reaction, corresponding to the equilibrium:

$$CaWO_4(\text{solid}) + Na_2CO_3(\text{solution}) \rightleftarrows Na_2WO_4(\text{solid}) + CaCO_3(\text{solid}).$$

may take place during the leaching of the cake.

This is confirmed by the fact that the tungsten concentration in the precipitate increases as the leaching time of the cake is increased.

According to the data of Zelikman and Ryabova, the equilibrium constant of the above reaction, expressed as the ratio of the concentrations by weight in the solution at 90°, i.e., $\frac{[Na_2CO_3]}{[Na_2WO_4]}$, equals 0.78 /2/.

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The value of the equilibrium constant may be used to calculate the minimum amount of sodium carbonate (over the stoichiometric amount) which must be taken in order to bring about quantitative dissolution of the tungsten.

The amount of Na_2CO_3 required for the formation of 294 g of Na_2WO_4 is 106 g. In order to retain the sodium tungstate in solution, it is necessary that the solution contain a certain amount of sodium carbonate, which may be calculated from the equilibrium constant:

$$\frac{[Na_2CO_3]}{294} = 0.78;\ [Na_2CO_3] = 294 \cdot 0.78 = 230\ \text{g}.$$

The minimum amount of sodium carbonate theoretically required is therefore 230 g + 106 g = 336 g, which is 3.17 times the stoichiometric amount. In practice, even larger amounts are required.

In order to make the scheelite decomposition process irreversible, quartz sand is added to the charge in an amount calculated to bind the calcium as the insoluble silicate:

$$CaWO_4 + Na_2CO_3 + SiO_2 = Na_2WO_4 + CaSiO_3 + CO_2.$$

Sodium carbonate most probably first reacts with the sand, yielding sodium silicate, which subsequently reacts with the calcium tungstate:

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2,$$
$$CaWO_4 + Na_2SiO_3 = CaSiO_3 + Na_2WO_4.$$

Thus, the charge used in the processing of scheelite concentrates consists of the finely divided concentrate, sodium concentrate (in a 50 to 100% excess over the theoretical amount), quartz sand and waste.

The furnaces employed for the fusion are of the type used in the fusion of the wolframite — sodium carbonate charge. The cake contains sodium tungstate, calcium silicate, sodium silicate, sodium salts of contaminants (molybdenum, arsenic, phosphorus, etc.) and the undecomposed fraction of the scheelite. It is processed by the method used to process the cake from wolframite concentrates. The processing of both types of concentrates is diagramatically shown in Figure 2.

Decomposition in autoclaves with aqueous solutions of sodium carbonate* /4, 20, 26/

The process is based on the reaction:

$$CaWO_4(\text{solid}) + Na_2CO_3(\text{solution}) \rightleftarrows Na_2WO_4(\text{solution}) + CaCO_3(\text{solid}).$$

---

* A soda leaching process of wolframite concentrates with sodium carbonate solutions in autoclaves has been recently developed /20/. In order to obtain an effective decomposition it is necessary that the CO_2 formed in the reaction

$$FeWO_4 + Na_2CO_3 + H_2O \rightarrow Fe(OH)_2 + Na_2WO_4 + CO_2$$

be continuously removed from the system.

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The studies of Maslenitskii have shown that at 180—200° the reaction proceeds at a satisfactory rate and to a satisfactory degree of completion.

If the solution temperature must be increased above the normal boiling point, the heating is done in autoclaves (hermetically sealed containers) and not in open vessels. When an aqueous solution is heated to 200° in an autoclave, its vapor pressure reaches 15 atm.

Syrokomskii and Maslenitskii /4/ were the first to develop a method for the decomposition of scheelite concentrates with sodium carbonate solutions in an autoclave. This method gives good results in the processing of both lean (containing up to 20% WO_3) scheelite concentrates and rich tailings (containing up to 5% WO_3) from enrichment plants, as well as ordinary concentrates. As compared with the fusion of scheelite concentrate with sodium carbonate and sand, the decomposition with sodium carbonate solution has the advantage of not requiring a furnace or the associated preparatory stages. The disadvantage of the autoclave process is that the consumption of sodium carbonate is high. The amount of sodium carbonate required for the quantitative decomposition of the scheelite concentrate depends on its WO_3 concentration. An amount 2.5 to 3 times the stoichiometric is required for the decomposition of rich concentrates. An amount 4 to 4.5 times the stoichiometric is required for the decomposition of lean concentrates (15 to 20% WO_3). The processing of the concentrates with sodium carbonate solutions is carried out in autoclaves of various types:

a) fitted with a mechanical stirrer and heated by means of spent steam;

b) heated and stirred by means of live steam; the mixing is accomplished by bubbling the steam through the slurry;

c) horizontal autoclaves, containing balls rotating with the charge. Heating is carried out by means of live steam (Figure 7).

Recent investigations have shown that the use of autoclaves containing milling equipment results in an increase in the rate of decomposition and a reduction in the sodium carbonate consumption (to 1.75 to 2.0 equivalents) in the processing of standard scheelite concentrates. This can be attributed to the abrasive action of the balls, which remove the $CaCO_3$ layer from the surface of the scheelite particles. However, the design of ball autoclaves is more complicated than that of other types.

The autoclaves are built of special nickel steel and ordinary carbon steels. Batch process is generally used in autoclave operation. An aqueous slurry containing the sodium carbonate and the scheelite concentrate (particle size 0.5 to 0.6 mm) is run from the mixer to the autoclave through a gravity-flow line (see Figure 7). When leaching is complete, the slurry is discharged from the autocalve into the evaporator, in which the pressure is lower than in the autoclave (i. e., about 1.5 to 2 atm) and in which the slurry boils vigorously and is thus rapidly cooled. The evaporator (Figure 7) consists of a cylindrical steel vessel with conical upper and lower ends. The slurry is fed from the autoclave into the center of the evaporator through a pipe. The steam formed passed through a splash-head and is discharged through a nozzle. The slurry is run-off through the lower nozzle. The lower end of the evaporator is protected against the thrust of the inflowing slurry stream by means of a guard made of armor-plated steel. The slurry from the evaporator passes into a collector and, from there, to the filtering and washing stages.

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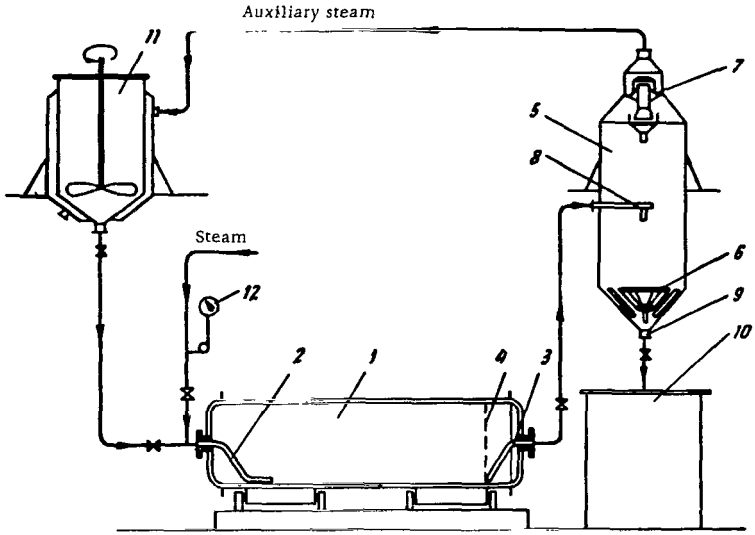

FIGURE 7. Autoclave processing of scheelite concentrates.

1—horizontal autoclave; 2—feed pipe (used also for the supply of steam); 3—discharge pipe; 4—perforated partition (if balls are used); 5—evaporator; 6—guard (armor-plated steel); 7—splash-head; 8—inlet of slurry; 9—discharge nozzle; 10—slurry collector; 11—reactor for the preparation of the slurry; 12—manometer.

As an illustrative example we have shown below the processing of standard scheelite concentrates containing 4 to 5% molybdenum (Figure 8) /29/. The process is designed to produce tungstic anhydride and molybdenum concentrate containing 57 to 61% Mo and about 2.5% WO_3.

Acid decomposition

The direct decomposition of scheelite concentrates with hydrochloric acid according to the equation:

$$CaWO_4 + 2HCl \rightleftarrows H_2WO_4 + CaCl_2.$$

is widely used in industrial processing of these concentrates (see Figure 9).

As a result of the decomposition, calcium chloride and other soluble impurities pass into the solution, while tungstic acid, together with silica and undecomposed scheelite remains in the residue. The technical grade tungstic acid thus obtained is purified by the ammoniacal method.

As compared with alkaline decomposition, decomposition with acids involves a smaller number of operations. Moreover, when employing the acid decomposition process, a substantial fraction of the impurities is removed already during the decomposition with hydrochloric acid.

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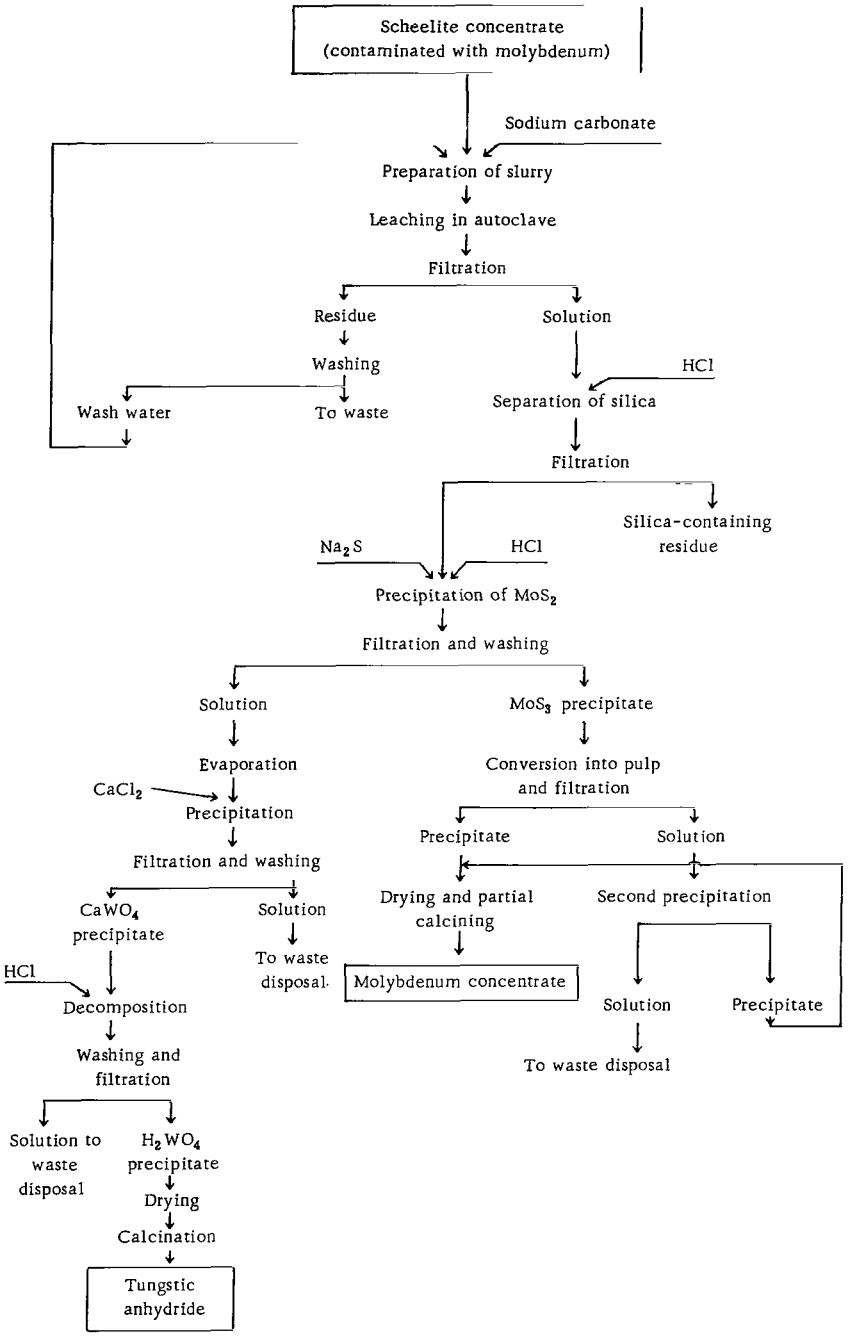

FIGURE 8. Processing of scheelite concentrates by the autoclave process.

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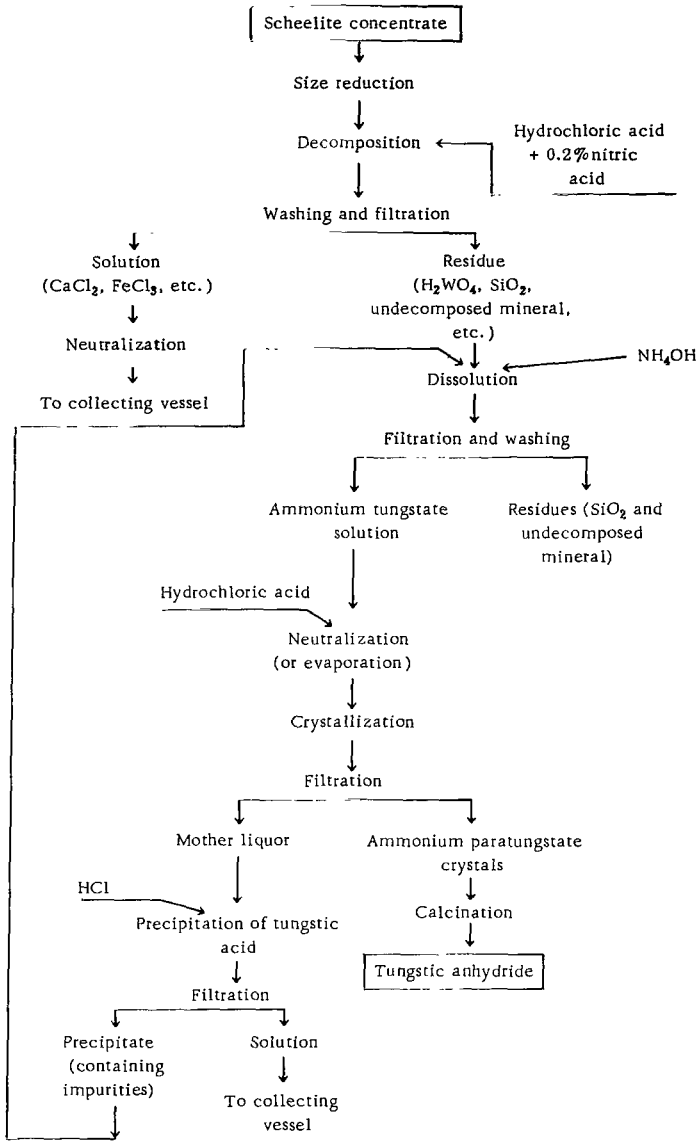

FIGURE 9. Processing of scheelite concentrates by the acid process.

Hydrogen sulfide liberated during the decomposition of sulfide impurities may bring about partial reduction of the tungstic acid to a blue-colored, lower-valency compound. This may be prevented by the addition of 0.2 to 0.5% nitric acid.

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The process is carried out in an iron reactor lined with rubber or some other acid-resistant material; the vessel is filled with concentrated hydrochloric acid (~ 250% of the stoichiometric amount) and nitric acid is added. The concentrate is then fed into the reactor. The process is carried out for 6 to 8 hours at 70 to 80° with stirring. The residue (which consists of tungstic acid, silica, and undecomposed mineral) is rinsed several times with hot water (as described on p. 23). The washed technical grade tungstic acid precipitate containing 2 to 3% impurities is forwarded to the purification state (see Figure 9).

One of the drawbacks of the acid decomposition method is the large consumption of hydrochloric acid. This may be counteracted by working in heated ball mills, in which the decomposition and the milling are conducted simultaneously, while the tungstic acid layer is removed from the surface of the scheelite particles /5/. This results in an increased rate of decomposition and a reduction of the acid consumption to 150% of the stoichiometric amount.

7. PURIFICATION OF TUNGSTIC ACID

The technical grade tungstic acid produced by one of the above methods may contain 0.2 to 3% impurities in the form of calcium and sodium salts, silica, molybdic acid, adsorbed iron, manganese and aluminum salts, phosphorus, arsenic and other compounds, and undecomposed scheelite (in the case of tungstic acid produced by the decomposition of scheelite concentrate).

The total concentration of SiO_2 and alkali and alkaline-earth metal salts (which together account for the bulk of the impurities) is expressed as the "chlorination residue". This is the residue obtained on chlorinating an accurately weighed amount of tungstic acid (or tungstic anhydride) with dry chlorine or HCl at 800°. The chlorination liberates the volatile chlorides of tungsten, iron, manganese, aluminum, phosphorus, etc. The residue contains SiO_2 and the alkali and alkaline-earth metal chlorides. The maximum permissible "chlorination residue" in tungstic acid or anhydride used for the production of tungsten wire is 0.1%; in the anhydride used for the production of tungsten carbide it is 0.1 to 0.15% (see Table 10).

Tungstic acid is usually purified by the ammonia process. Tungstic acid dissolves readily in ammonium hydroxide solutions with formation of a solution of ammonium tungstate. Most of the impurities, silica, iron and manganese hydroxides, and calcium in the form of $CaWO_4$ remain in the residue. The tungsten is precipitated from the ammoniacal solution as tungstic acid or ammonium paratungstate.

Dissolution of H_2WO_4 in ammonium hydroxide solution

When tungstic acid is dried at temperatures not exceeding 170°, it readily dissolves in aqueous solutions of ammonium hydroxide. When dried at higher temperatures, the acid loses its chemically combined

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water and becomes less readily soluble in ammonium hydroxide. Ignition of H_2WO_4 at 500° causes a complete loss of water and leads to the formation of tungstic anhydride, which is only sparingly soluble in ammonium hydroxide.

Tungstic acid is sent to the dissolution stage in the form of a suspension (1 kg of WO_3 per 1.5 liter of water) preheated to 80 to 85°. The suspension is poured into a reactor containing a 25% solution of ammonium hydroxide (the consumption of ammonium hydroxide (d = 0.91) is 115 liters per 100 kg of WO_3). The ammoniacal solution is left to settle for 8 to 12 hrs and is separated from the residue (SiO_2, CaO, etc.) by decantation. The density of the solution is 1.29 to 1.30, which corresponds to a WO_3 content of 320 to 330 g/l.

The ammoniacal solution is free of the bulk of the impurities originally present in the technical grade tungstic acid. However, it may contain molybdenum, sodium, magnesium and iron salts.

Isolation of tungsten from ammoniacal solutions

Precipitation as H_2WO_4. This is carried out in the same way as the precipitation of the acid from Na_2WO_4 solutions (p. 22).

To obtain high purity H_2WO_4 the product is redissolved in ammonium hydroxide and reprecipitated by acid.

Isolation of the paratungstate. The paratungstate is isolated from ammoniacal solution either by evaporation or by neutralization of the solution.

The evaporation method. When an ammoniacal solution is evaporated, a part of the ammonia is liberated and ammonium paratungstate is formed. The platelet-shaped modification corresponding to the formula $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$ crystallizes out of solution on cooling. The crystals are separated first by filtration and then by centrifuging, and are then rinsed with cold water and dried. The solution is evaporated to a definite residual volume (calculated to result in the separation of about 80% of the tungsten) in continuous or batch evaporators. The crystallization of a larger fraction of the tungsten is not recommended, since it would result in contamination of the crystals with impurities. The degree of purification obtained by the ammoniacal method is shown in Table 8.

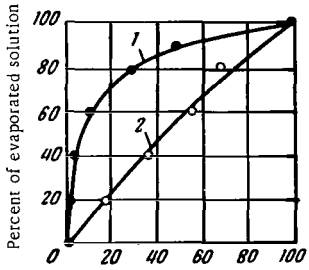

FIGURE 10. Variation of the amount of crystallized ammonium paramolybdate (1) and paratungstate (2) with the degree of evaporation of the solution.

The tungsten in the mother liquor (containing an increased amount of impurities) is precipitated as $CaWO_4$ or H_2WO_4 and these are appropriately recycled for re-processing.

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If the starting solution of ammonium tungstate contains molybdenum, ammonium paramolybdate crystallizes out together with ammonium paratungstate. The paratungstate is less soluble than the paramolybdate; hence, molybdenum may be separated from tungsten by fractional crystallization.

TABLE 8

Efficiency of the ammoniacal purification of tungstic acid
(according to Smithells /1/)

Product	Total impurity content, % of WO_3
Initial tungstic acid (technical grade)	3.2
Initial solution of H_2WO_4 in NH_4OH	0.2
H_2WO_4 precipitated from the initial solution	0.25 (small increase, caused by the presence of iron in the hydrochloric acid)
Second solution of H_2WO_4 in NH_4OH	0.07
Ammonium paratungstate crystals after evaporation and crystallization	0.04

The variation of the amount of crystallized ammonium paramolybdate and paratungstate with the degree of evaporation of the solution is shown in Figure 10 /1/. For instance, the evaporation of 60% of the liquid results in the precipitation of 55% of the tungsten and only 12% of the molybdenum originally present in the solution. Thus, the first fractions of ammonium paratungstate crystals may contain only traces of molybdenum and may be used for the production of pure tungsten. The subsequent fractions crystallized from the mother solution have a larger molybdenum content.

The neutralization method. Needle-shaped ammonium tungstate (with 11 molecules of water of crystallization) is formed when a cold ammoniacal solution is carefully neutralized; the overall reaction is:

$$12(NH_4)_2WO_4 + 14HCl + 4H_2O = 5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O + 14NH_4Cl.$$

The solution is neutralized by a slow addition of HCl; continuous stirring is required in order to prevent localized overacidification, which may lead to the formation of the metatungstate. The degree of precipitation is strongly affected by the pH, the optimum pH value being between 7.3 and 7.4.

The solution is allowed to stand for a prolonged time (up to 24 hours) when 85 to 90% of the tungsten precipitate as the needle-shaped paratungstate. The salt is usually very pure. For the sake of additional purification it is sometimes treated with hydrochloric acid to yield tungstic acid:

$$5(NH_4)_2O \cdot 12WO_3\ 11H_2O + 10HCl = 12H_2WO_4 + 10NH_4Cl + 4H_2O.$$

For this purpose, the salt is introduced in small amounts into a reactor containing concentrated HCl and the resultant solution is heated to boiling.

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8. PRODUCTION OF TUNGSTEN TRIOXIDE AND QUALITY CONTROL

Tungsten trioxide is produced by ignition of tungstic acid or ammonium paratungstate:

$$H_2WO_4 \rightarrow WO_3 + H_2O,$$
$$5(NH_4)_2 \cdot 12WO_3 \cdot nH_2O \rightarrow 12WO_3 + 10NH_3 + (n+5)H_2O.$$

Tungstic acid is completely dehydrated at 500° while ammonium tungstate decomposes quantitatively above 250°.

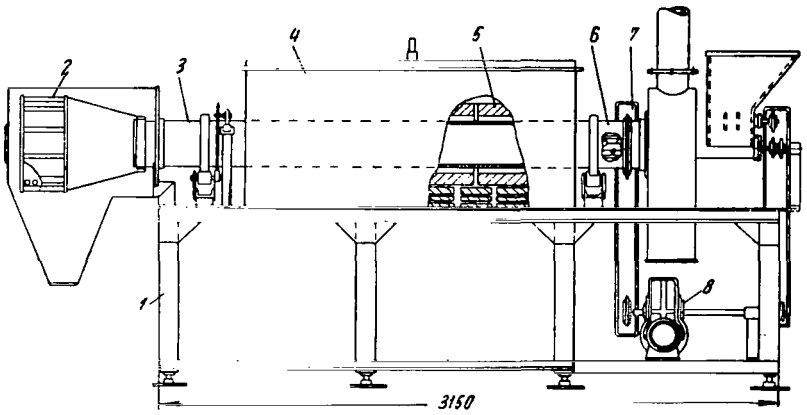

FIGURE 11. Rotating-tube furnace for the ignition of tungstic acid.

1—furnace framework; 2—drum sieve; 3—stainless steel tube; 4—jacket; 5—furnace chamber; 6—screw feeder; 7—drive; 8—reduction gear.

The tungstic acid is ignited to 750 to 850° in a rotary electric furnace. The furnace (Figure 11) consists of a stainless steel tube located in a heating chamber lined with refractory plates with grooves containing nichrome heaters. The chamber is thermally insulated and enclosed in an iron jacket. The tube is rotated by means of a motor and reduction gear. The tungstic acid is charged continuously from the hopper into the furnace by means of screw feeders. The discharge end of the tube is fitted with a drum sieve with 1.2 to 3 mm holes. The slope of the furnace may be changed with the aid of a special device. The vapors generated in the furnace are drawn out through a dust-collecting device (bag filters).

Not only the purity of the tungstic anhydride, but also its particle size (which depends on the conditions under which the tungstic acid is formed and on the ignition temperature) is of great importance for the production of tungsten or tungsten carbide. The particle size of any powder may be described as its bulk weight. This term is defined as the weight of a unit volume of the loose (uncompressed) powder; it is usually expressed in grams per cubic centimeter. The bulk weight of fine powders is lower than that of coarse powders. This is attributed to the fact that fine powders have a larger total surface and the action of cohesion (friction)

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forces between the particles is stronger than in coarse powders, and prevents the powder from becoming more densely packed.

A new and more accurate method for controlling the physical structure of the powder has been recently introduced; it is based on the measurement of the amount of adsorbed methanol vapors (the larger the specific surface of the powder, the higher the degree of adsorption). The device shown in Figure 17 has been developed in the USSR for this purpose.

As is evident from Table 9, the methanol adsorption method is more sensitive than the bulk density method.

TABLE 9

Variation of the physical properties of tungstic anhydride powder with the temperature of ignition of tunstic acid

Temperature, °C	Methanol adsorbed, mg/g	Bulk density, g/cm^3	Temperature, °C	Methanol adsorbed, mg/g	Bulk density, g/cm^3
550	0.99	0.61	750	0.14	0.67
600	0.72	0.62	800	0.06	0.73
650	0.59	0.62	850	0.04	0.79
700	0.47	0.63			

TABLE 10

Approximate specification for technical grade tungsten trioxide

Component	Concentration, %	
	for hard alloys	for metallic tungsten
Tungsten trioxide	$\geq$ 99.8	$\geq$ 99.95
Molybdenum	$\leq$ 0.1	$\leq$ 0.02
Arsenic	$\leq$ 0.015	$\leq$ 0.02
Phosphorus	$\leq$ 0.025	$\leq$ 0.01
Sulfur	$\leq$ 0.015	$\leq$ 0.02
Chlorination residue	0.10 — 0.15	*0.10*
Calcium oxide	—	$\leq$ 0.01
Sesquioxides	$\leq$ 0.04	$\leq$ 0.01
Weight losses upon ignition	0.5	0.05

The particle size of tungstic anhydride prepared from ammonium paratungstate is usually larger than that of the anhydride prepared from tungstic acid.

The purity specifications for technical grade tungsten trioxide are shown in Table 10.

9. COSTS OF PRODUCTION OF TUNGSTIC ANHYDRIDE

An analysis of the costs of production makes it possible to reduce the expenditure involved.

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The approximate cost of producing one ton of tunstic anhydride from scheelite concentrates by the sodium carbonate method (see Figure 2) is shown below, as % of the total cost f. o. b. factory:

Raw material — scheelite concentrate	83.0
Reagents-sodium carbonate, quartz sand, hydrochloric acid, calcium chloride, etc.	9.7
Auxiliary materials — filter cloth, etc.	0.2
Energy consumption — electrical, fuel, steam, water	1.7
Wages with benefits	2.0
Overheads	3.4
Total	100.0

The main item in the cost price (83.0%) is the raw material. Hence, the cost of tungstic anhydride will be reduced in the first place by reducing the consumption of scheelite concentrate required to produce one ton of tungstic anhydride by reducing the losses occurring in individual processing stages.

The total degree of extraction of WO_3 from the concentrate into the finished product (tungstic anhydride) is now 93 to 95%. The approximate losses at each stage are shown below in %:

Size reduction and charge mixing	0.5
Fusion (loss by dust entrainment)	0.5
Leaching and filtration	1.0 to 2.0
Purification of solution	0.5
Precipitation of artificial scheelite	0.5 to 1.0
Production of tungstic acid and washing	1.0 to 2.0
Drying and ignition (dust entrainment)	0.5

In order to increase the degree of extraction strict control of all production stages should be maintained to reduce mechanical losses caused by comminution of the concentrate and transport of the solutions, efficient dust trapping during ignition of the tungstic acid should be ensured and the tungsten should be recovered from the wash liquids from the calcium tungstate decomposition stage and from other wastes. Although the relative contribution of the wages to the cost price is not large, labor should nevertheless be saved by further mechanization and automation of the production process. This will also result in decreased losses and improvement of the quality of the tungstic anhydride.

10. PRODUCTION OF METALLIC TUNGSTEN

Because of its high melting point tungsten is produced from its compounds as powder which is converted into metal parts by using the methods of powder metallurgy. The possibility of producing tungsten parts by modern vacuum melting methods (electron beam or arc melting) has been investigated over recent years.

Tungsten powder may be prepared by the reduction of tungsten compounds (tungsten trioxide, tungstic acid, or its salts) with different

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reducing agents at relatively low temperatures (800 to 1200°). Powders of various degrees of purity are obtained depending on the purity of the starting material and the reducing agent used. The highest purity standards must be met by powders used in the production of ductile tungsten.

Reduction may be carried out with the aid of hydrogen, carbon, metals (aluminum, silicon, sodium, etc.) or by an electrolytic method. The processes used in industry are based on the reduction of tungsten trioxide by hydrogen or carbon; hydrogen is the only reducing agent used in the production of ductile tungsten. The standards for tungsten powder specify not only the degree of chemical purity, but also the physical structure of the powder (particle size and shape, size distribution, degree of conglomeration). These characteristics determine the behavior of tungsten when the powder is subsequently compacted and the behavior of the resulting metal parts. The physical structure of the metallic powder depends on the structure of the starting material and the conditions of the reduction.

11. REDUCTION OF TUNGSTEN TRIOXIDE BY HYDROGEN

Physicochemical conditions of the reduction process

The reduction of tungstic anhydride by hydrogen is a four-stage process /6/ corresponding to the stepwise formation of four tungsten oxides, WO_3, $WO_{2.9}$ (or $W_{10}O_{29}$), $WO_{2.75}$ (or W_4O_{11}) and WO_2 according to the following reactions:

$$10WO_3 + H_2 \rightleftarrows W_{10}O_{29} + H_2O; \quad (1)$$

$$2W_{10}O_{29} + 3H_2 \rightleftarrows 5W_4O_{11} + 4H_2O; \quad (2)$$

$$W_4O_{11} + 3H_2 \rightleftarrows 4WO_2 + 3H_2O; \quad (3)$$

$$WO_2 + 2H_2 \rightleftarrows W + 2H_2O; \quad (4)$$

The overall reaction is:

$$WO_3 + 3H_2 \rightleftarrows W + 3H_2O.$$

These reactions are reversible and their course is determined by the equilibrium constants

$$K_p = \frac{p_{H_2O}}{p_{H_2}},$$

where p_{H_2O} and p_{H_2} are the equilibrium partial pressures of hydrogen and water vapor.

The effect of temperature on the equilibrium constants of the above reactions is expressed by the following equations /6/:

$$\lg K_{p_1} = -\frac{3266.9}{T} + 4.0667; \quad (1)$$

$$\lg K_{p_2} = -\frac{4508}{T} + 5.1086; \quad (2)$$

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$$\lg K_{p_2} = -\frac{904}{T} + 0.9054; \quad (3)$$

$$\lg K_{p_4} = -\frac{2325}{T} + 1.650. \quad (4)$$

The $\log K_p - \frac{1}{T}$ relationship is linear as shown graphically in Figure 12. The graph showing the variation of K_p with temperature indicates the optimum conditions for the reduction of tungsten oxides.

Each value of $\log K_p$ on the ordinate corresponds to a fixed water-vapor-to-hydrogen ratio in the gas mixture. Let us assume that a given temperature (e.g., 850°) the gas composition corresponds to point A. No reduction of WO_3 takes place at this composition as the water vapor concentration in the gas is above the equilibrium value. In order to effect the reduction, it is necessary to reduce the concentration of water vapor by drying the hydrogen. At 850° the reduction of WO_2 to tungsten could proceed only if the humidity of the hydrogen (i.e., the $\frac{p_{H_2O}}{p_{H_2}}$ ratio is below the value corresponding to point B.

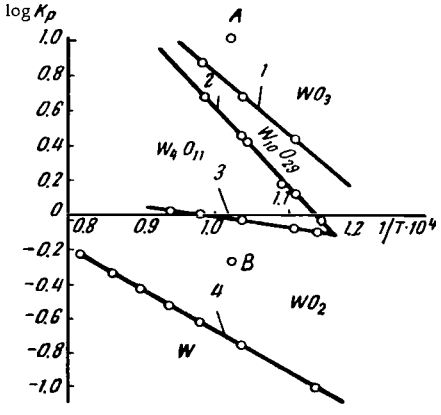

FIGURE 12. Variation of the equilibrium constant of the reduction of tungsten oxides by hydrogen with temperature.

Consequently, either tungsten or some of its oxides may be the stable form at a given temperature, depending on the composition of the gaseous phase (water-vapor-to-hydrogen ratio). Thus, WO_3 is the stable form at 700° and at a H_2 concentration below 23% in the gaseous phase (WO_3 cannot be reduced under these conditions); the oxide W_4O_{11} is the stable form when the H_2 concentration in the gas is between 23 and 45%; WO_2 is the stable form at an H_2 concentration of 45 to 73% and metallic tungsten at a hydrogen concentration above 73%. The reduction temperature decreases as the moisture content of the hydrogen is reduced.

Thoroughly dried hydrogen must be used in order to ensure a sufficiently high rate of the reduction process.

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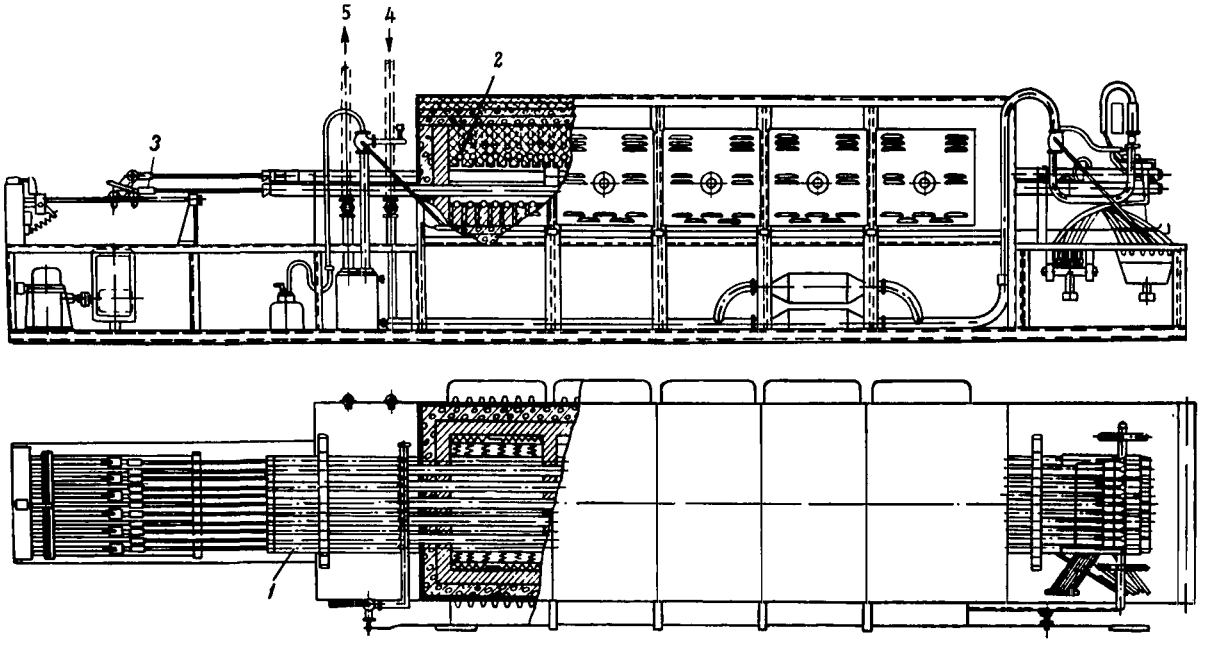

FIGURE 13. An eleven-tube hydrogen reduction furnace.

1—tubes; 2—heaters; 3—pushers; 4—hydrogen inlet pipe; 5—hydrogen discharge pipe.

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Reduction furnaces

The reduction of tungstic anhydride by hydrogen is carried out in stationary multitube furnaces (with continuous or batchwise transport of the material undergoing reduction along the length of the furnace) or in rotary tube furnaces. Multitube electrical furnaces are the ones most commonly used.

The construction of such a furnace is shown in Figure 13 /3/. The furnace comprises 11 tubes in two horizontal rows (6 in the lower and 5 in the upper row); the tubes are made of stainless chromium-nickel steel. The tube diameter is 50 to 70 mm, and the tube length is 5 to 7 m. The tubes are enclosed in an iron jacket which is lined on the inside with a thermally insulating material; asbestos sheet, diatomaceous or chamotte bricks or asbestos cement plates. Directly below and above the tubes there is a layer of molded earthenware tiles with grooves accommodating spiral nichrome-wire heaters, 4.5 to 5 mm in diameter.

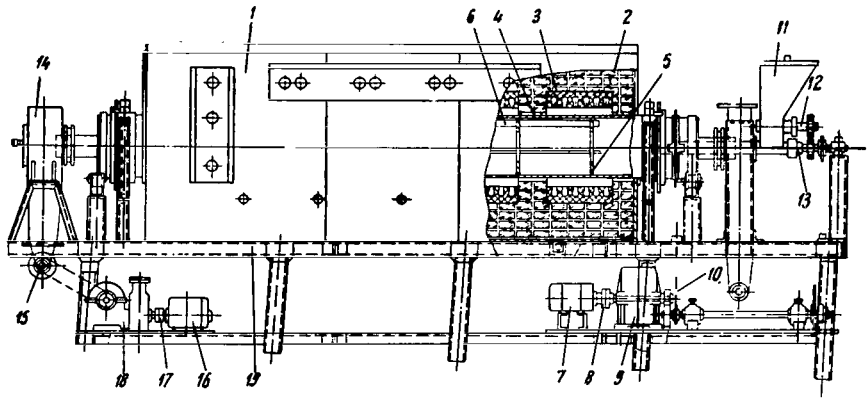

FIGURE 14. Rotary-tube furnace for the reduction of tungstic anhydride with hydrogen.

1—furnace casing; 2—lining; 3—shaped ceramic lining; 4—steel tube; 5—diaphragms; 6—longitudinal shelves; 7—motor; 8—pulley; 9—reduction gear; 10—chain; 11—charging hopper; 12—loosening device; 13—screw feeder; 14—discharge hopper; 15—discharging device; 16—electric motor; 17—coupling joint; 18—reduction gear; 19—base.

There are several (three or five) temperature zones within the furnace, whose total length is about 4 m. The furnace power ranges from 30 to 50 kw. The boats containing the tungsten trioxide are moved along the tube with the aid of a mechanical pusher. The pusher mechanism, consisting of a gear box, a screw, a carriage, and an electric motor, is mounted on a special table next to the entry of the furnace. The rate of movement of the boats in the furnace may be varied from about 5 to 30 mm/minute. The discharge end of the furnace is fitted with a cooling device in order to cool boats emerging from the hot zone of the furnace. Hydrogen is fed from a collector into the furnace tubes. The spent hydrogen from the tubes is collected at the charging end of the furnace and is purified, regenerated, and recycled.

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In addition to the multitube furnaces described above, continuous rotary drum electrical furnaces are beginning to be used in the USSR /3/. Such furnaces have some advantages — high productivity, the elimination of manual labor, and lower electrical energy consumption per unit weight of product.

The electrical furnace designed by Babich (Figure 14) consists of a stainless steel tube (400 mm in diameter and 4 m long) supported by two rollers and rotated by means of electric motor and a transmission system. The tube is placed in a heating chamber.

The tube contains diaphragms 5 with an opening in their center and longitudinal fins 6 made of angle iron and welded to the tube. The diaphragms prevent the material, which is of a rather high density from slipping along the tube. The material is thus kept in a reducing atmosphere in the heated zone for a longer time. The longitudinal fins disperse the material and thus promote better contact between the solid particles and the hydrogen. The forward part of the furnace accommodates the charging hopper 11 with a loosening device 12 and a screw feeder 13. The end of the furnace is connected to the discharge hopper 14 with a screw-type discharging device 15. The furnace casing is mounted on a base 19 made of angle iron, sloping at 2 to 4° in the discharge direction.

The length of the furnace is divided into four thermal zones; the temperature of each zone is regulated automatically.

Hydrogen enters the tube through the discharge hopper of the furnace and the direction of its flow through the furnace is opposite to that of the material; the hydrogen leaves the furnace at the upper end and is subsequently regenerated.

The furnace turns at about 2 rpm. The hydrogen stream moves at a rate of 18 to 20 m^3/hr.

Supply of hydrogen to the furnace. The hydrogen fed to the furnace must be thoroughly dried and purified to remove oxygen and water vapor.

The use of electrolytic hydrogen (i. e., hydrogen prepared by electrolyzing water) is preferable when pure tungsten powder is required. A little sodium hydroxide is added to the water in order to increase its conductivity. The hydrogen produced in electrolytic cells is collected in gas holders from which it is fed into the furnace through a system of pipes after passing through a purification system.

The oxygen is removed by passing the gas through a vertical furnace packed with a catalyst (copper turnings or a special Fe — Cu — Ni catalyst) heated to 600 to 650°. On the surface of the catalyst the oxygen combines with hydrogen, yielding water. The water vapor is removed when the hydrogen is passed through a drying system consisting of columns packed with a moisture-absorbing substance (NaOH, $CaCl_2$, silica gel, P_2O_5).

The drying is carried out most conveniently with the aid of silica gel (dried and granulated silicic acid) which has a high sorption capacity. The silica gel is regenerated by heating to 180°. There is usually a heater on the column containing the silica gel. After a certain period, the column is closed off and the silica gel is regenerated.

Dried hydrogen is supplied to all tubes of the furnace from the hydrogen delivery line through nozzles cut in the discharge ends of the tubes.

In order to reduce the hydrogen losses during reduction, the spent hydrogen leaving the furnace is regenerated in a special regeneration

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setup (Figure 15). At the exit from the furnace 1 the spent hydrogen enters the collector 2, and passes through the trap 3 into condenser 4. The trap is partially filled with water and the hydrogen delivery tube from the collector is immersed in the water. A fraction of the water vapor condenses in the trap. The condensation is completed in the water-cooled condenser tube 4. The condensate is discarded. The hydrogen leaving the condenser is mixed with fresh oxygen-free hydrogen from the supply line and the mixture is passed through the drying tower 5 which contains one of the desiccants mentioned above. The moisture-absorbing particles entrained with the gas stream are trapped in the bag filter 6.

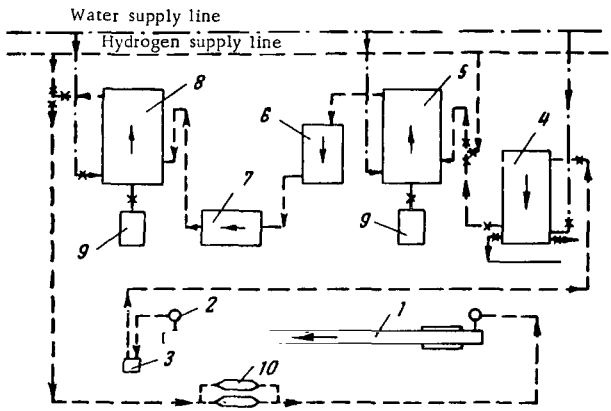

FIGURE 15. Hydrogen regeneration scheme.

The dried hydrogen enters the compressor 7 where the required overpressure is produced (the required pressures in the system are: 100 mm water before entering the compressor and a maximum of 1000 mm water in the compressor). From the compressor the hydrogen passes into the drying tower 8 (with a water supply tank 9) for a more thorough drying. From the tower 8 the hydrogen is fed into the furnace through the explosion extinguishers 10.

The explosion extinguisher consists of two metallic cylinders filled with thin tungsten wire; the cylinders serve to extinguish explosions and to disconnect the furnace from the regeneration setup and the hydrogen supply line.

The fresh hydrogen delivered from the supply line replenishes the volume lost in the reduction and during charging and discharging of the boats.

The reduction process

In practice, the reduction of tungstic anhydride is a two-stage process. This is due to the volume decrease (by a factor of about 3) of the charge in the boats during the reduction of WO_3 to W (the density of WO_3 is 7.2 while that of W is 19.3). Because of this volume decrease the boats would travel most of their path only partially filled in a one-stage process.

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The first stage consisting of the reduction to WO_2 is carried out in one group of furnaces while the second stage (the reduction from WO_2 to W) in another.

In the production of a special type of tungsten, which is used to manufacture non-sagging wire for lamp filaments, the two-stage reduction process may be used for the preparation of tungsten powder with a more diversified particle size. For this purpose, the boats entering the second reduction stage are loaded with a mixture of tungsten dioxide and tungstic anhydride at various ratios (25 to 50% WO_3). The reduction conditions selected in accordance with the required particle size of the tungsten powder. Some two-stage reduction conditions are listed in Table 11.

TABLE 11

Conditions during the reduction of tungstic anhydride by hydrogen

Reduction stage	Conditions				Purpose
	maximum temperature, °C	load in boat, g	rate of motion of the boat, cm/hr	hydrogen consumption m^3/hr	
First.....	700—720	189—200	100	0.5—0.6	Production of fine tungsten powder
Second.....	800—820	200—250	100	2—3	
First.....	720—750	200—250	200—300	0.6—0.8	Production of coarser powders
Second.....	850—900	500—600	100	1.7—2.0	

The fine tungsten powder (brand VCh) prepared under these conditions has the following granular composition: 56 to 60% below 0.6 μ; 38 to 40% in the 0.6 to 1.2 μ range; 3 to 5% in the 1.2 to 1.8 μ range. The bulk density is 2.2 to 2.5 g/cm^3.

The particle size of tungsten powder depends on a number of factors; the most important of them are the reduction temperature, the particle size of the starting oxides, and the rate of flow of hydrogen.

The effects of the temperature and the particle size of the starting oxides are interdependent. Coarse tungstic anhydride cannot be used for the production of fine powder, but fine powder may be used for the production of coarse tungsten powder /28/. This is due to the growth of oxide particles, whose rate increases with the temperature. The stronger such growth is exhibited by WO_3 particles, and the weakest by WO_2 particles. Moreover, the finely divided oxides grow more rapidly than the coarse ones. For instance, WO_3 particles with a size below 1 μ show a noticeable growth rate at 400°, and grow rapidly at 850°. When the particle size is increased from 1 to 5 μ, the growth of the WO_3 particles only starts at 600 to 800°.

It has been established (by observations made during the manufacturing process) that the formation of coarse particles of tungsten powder during the reduction of tungstic anhydride is mainly favored by:

1) high reduction temperature;
2) steep temperature gradient along the tube;
3) high rate of advance of the WO_3 boats in the tube;
4) thick WO_3 layer in the boats;
5) low hydrogen flow rate;
6) high moisture content in the hydrogen fed to the furnace.

Meerson showed that the effect of all these factors on the increase in the particle size of the tungsten powder may be attributed to the considerable vapor pressure of tungsten oxides at the reduction temperatures, taking into account that WO_3 is the most volatile /2/.

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The vapor pressure over fine particles is higher than over coarse particles; this can be attributed to the accumulation of surface energy in fine particles. Hence, at high temperatures (~ 800°) the WO_3 particles grow because of the vaporization of fine particles and the condensation of the vapors on the larger particles.

The tungstic anhydride not reduced in the low-temperature zone enters the high-temperature zone of the furnace. At temperatures above 600 to 700° the WO_3 is partially vaporized and reduced to WO_2 on the surface of the previously formed coarse WO_2 crystals, thus assisting the further growth of those crystals.

The first three factors favor the entry of unreduced WO_3 into the high-temperature zone. The remaining three factors (the increased height of the layer, the low flow rate of hydrogen, and the increase in its moisture content) have the same effect since they diminish the reduction rate and thus favor the entry of a large fraction of the WO_3 into the high-temperature zone.

By varying the factors mentioned above, it is possible to vary both the average particle size of the tungsten powder and the size distribution of the particles.

Control of the particle size of tungsten powder

A routine control of the particle size of tungsten powder is necessary to see that it meets standard specifications. Direct and indirect particle-size determination methods are used in the control of the particle size of fine powders (below 10 μ).

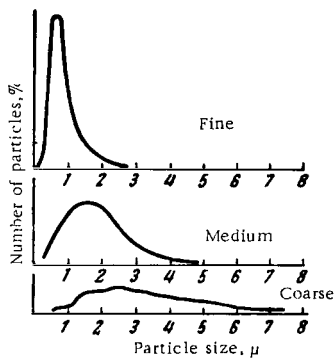

FIGURE 16. Curves showing the size distribution of tungsten powder.

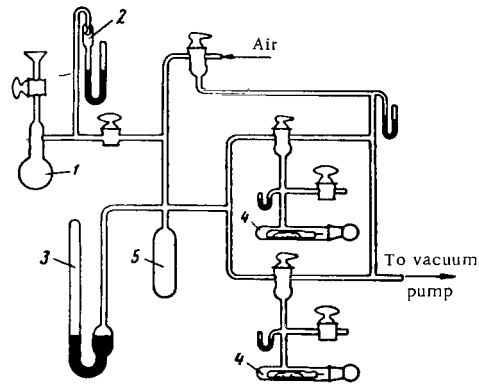

FIGURE 17. Apparatus for the measurement of the adsorption of methanol.

1—flask, "generator" of methanol vapor; 2—manometer for measurement of the methanol vapor pressure; 3—manometer for accurate measurement of the pressure within the system; 4—test tubes containing the powder; 5—glass container—receiver.

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Direct determination of the particle size is carried out by means of a statistical microscopic method, as follows: a sample of the powder is mixed and triturated with a solution of turpentine in turpentine oil and a drop of the mixture is placed on a slide on a microscope fitted with an eyepiece scale (or an eyepiece hairline). The results of several measurements (the total number of measured particles must be not less than 200 to 300) are used to calculate the distribution (in percent) of the particles by size (in microns) (Figure 16).

The indirect methods for determining the granule size composition of the powder include the determination of the bulk density and the determination of the relative specific surface of the powder. The bulk density is the weight of a unit volume of the loose (uncompressed) powder. It depends not only on the particle size and the size distribution of the particles, but also on their shape and the degree of roughness of their surface. Nevertheless, the particle size remains the most important factor as a rule, the larger the particles, the higher the bulk density of the powder.

Another method which is used in the Soviet Union for the quality control of tungsten powder is the measurement of the relative specific surface of the powder. The relative specific surface is obtained from measurements of the adsorption of methanol vapor (CH_3OH) or the gas permeability.

The apparatus used for measuring the adsorption of methanol is shown in Figure 17. The amount of adsorbed methanol is calculated from the difference in the methanol vapor pressure before and after adsorption. The amount of adsorbed methanol (in mg/g powder) is used as a measure of the relative specific surface of the powder. The finer the powder, the larger is its specific surface and the higher the amount of the adsorbed methanol vapor.

The method of gas permeability, developed by Deryagin, is based on the measurement of the rate of passage of air through a powder layer of a given thickness.

12. REDUCTION OF TUNGSTEN TRIOXIDE BY CARBON

Tungstic anhydride may be reduced by carbon where the presence of carbon in tungsten is permissible, e.g., in the production of hard alloys.

Physicochemical conditions for carbon reduction

The overall reaction of the reduction of tungstic anhydride by carbon is given by the equation:

$$WO_3 + 3C = W + 3CO.$$

In reality, the reduction proceeds through intermediate stages in which lower oxides are formed (as in the reduction with hydrogen). The main reducing agent is carbon monoxide (CO) rather than carbon; it reduces tungsten oxide as follows*:

$$4WO_3 + CO \rightleftarrows W_4O_{11} + CO_2, \qquad (1)$$

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* It is probable that there are actually four reduction stages, as in the reduction with hydrogen.

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$$W_4O_{11} + 3CO \rightleftarrows 4WO_2 + 3CO_2, \quad (2)$$

$$WO_2 + 2CO \rightleftarrows W + 2CO_2. \quad (3)$$

The carbon dioxide formed in the reaction reacts (at the reaction temperature) with the carbon in the charge as follows:

$$CO_2 + C \rightleftarrows 2CO. \quad (4)$$

The equilibrium constant of these four reactions is the ratio of the partial pressures of CO and CO_2 :

$$K_p = \frac{p_{CO_2}}{p_{CO}}.$$

The variation of log K_p with temperature is given by the following equations:

$$\log K_{p_1} = \frac{1555.5}{T} - 1.1427,$$

$$\log K_{p_2} = \frac{1029}{T} - 0.7884,$$

$$\log K_{p_3} = \frac{321.6}{T} - 0.0647.$$

Figure 18 shows the equilibrium composition of the gaseous phase (the CO content is in percent) as a function of the temperature, for the four reactions written above. The CO equilibrium pressure curve for the reaction WO_2—W intersects the curve of CO equilibrium pressure over carbon at about 750°. At that temperature, the CO has the same equilibrium pressure in both reactions.

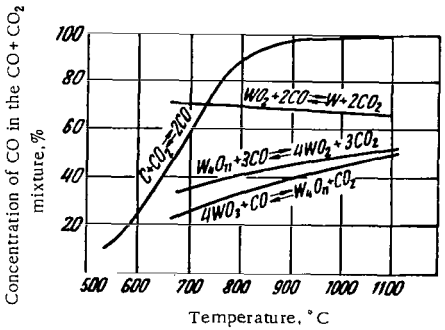

FIGURE 18. Equilibrium composition of the gaseous phase (CO/CO_2) as a function of temperature.

Below 750° the WO_2 cannot be reduced to W since the equilibrium pressure of CO over C is lower than the equilibrium pressure in the reduction of WO_2. In order to create a high concentration of CO in the gaseous phase and to accelerate the reduction process it is desirable to carry out the process at high temperatures (above 1000°) where the gaseous phase consists almost exclusively of carbon monoxide.

In contrast to the reduction of WO_3 by hydrogen, the reduction by carbon produces a fine tungsten powder even when high temperatures are employed (1400 to 1500°) and the charge is introduced rapidly into the high-temperature zone of the furnace. The charge must not remain in the high-temperature zone for a longer time than that required for a quantitative reduction, or sintering of the powder particles will occur.

The growth of tungsten particles during the reduction with carbon is inhibited by the presence of a thin layer of carbon black on the surface of the oxide particles. Because of the adsorption capacity of the carbon black, the WO_3 and lower oxide vapors which are formed at high temperatures in the pores of the charge are reduced mainly on the surface of the carbon black particles rather than on the surface of the primarily formed crystals of reduced tungsten. Such reduction is favored by the fact that even if the average concentration of CO_2 in the reaction space at high temperatures is quite low, it is still lower on the surface of the carbon black particles and the concentration of the reducing agent (gaseous CO) is at maximum.

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Industrial reduction of WO_3 by carbon

The tungstic anhydride used for the production of hard alloys must contain 99.85 to 99.9% WO_3.

The reduction of WO_3 is carried out by using pure brands of carbon black, such as lamp black, or gas black, whose ash content is only a few hundredths of one percent.

Usually, the amount of carbon added to the charge is equal to the stoichiometric (13.9%). This ensures that the C content in the reduced powder is low (i.e., does not exceed 0.5%).

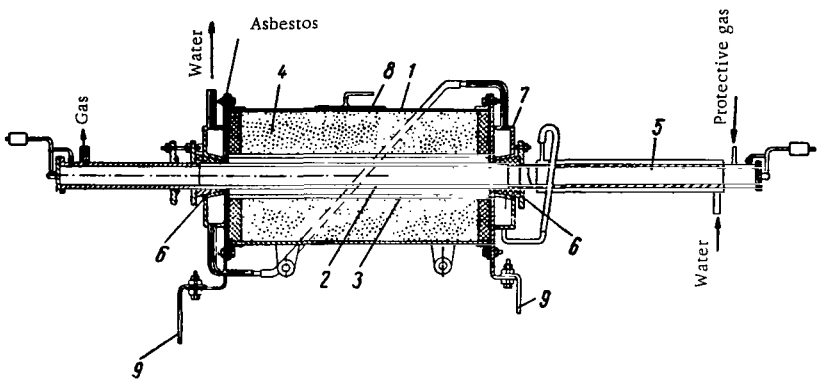

FIGURE 19. Carbon tube furnace.

1—casing; 2—graphite (or carbon) heating tube; 3—tubular screen; 4—carbon-black packing; 5—cooler; 6—contact cones; 7—current leads; 8—hatch for carbon black; 9—bus bars.

The WO_3 and the lamp black are mixed in ball mills, pug mills, or some other type of mixers for granulated substances. The mixture is swaged in carbon dies or compressed into cylindrical bricks.

The reduction is carried out in carbon tube furnaces (Figure 19). A graphite or carbon tube serves both as the heater and as the furnace space. The tube is 1000 to 1500 mm long and 75 to 100 mm in diameter. As a result of the low mechanical strength of graphite, it is necessary to use thick-walled tubes; hence, the electrical resistance of the heater is quite low. For this reason, the furnace requires a high current at a low voltage (15 to 25 V). The current is supplied through copper busbars to water-cooled contacts with conical openings in the center. Intimate contact between the carbon tube of the furnace and the current input is produced with the aid of graphite, copper, or cast-iron clamp cones of various types. Either carbon black or crushed coal is used as the thermal insulator.

The furnace is contained within an iron casing fitted with openings for the introduction and discharge of the thermal insulation packing. In order to facilitate the replacement of a burnt-out heater, some types of furnaces have the heater tube installed within a carbon tube screen (Figure 19). A cooler is connected directly to the graphite tube.

Using a furnace of the above type, a temperature of more than 2000° may be obtained with a 20 to 50 kw heater. The reduction is carried out at 1450 to 1550°. The molds containing the charge or the pressed briquettes move continuously along the furnace tube and remain in the hot zone for 40 minutes or one hour. The reduction yields friable gray blocks which are crushed and sifted.

The tungsten contains 0.1 to 0.5% carbon and 0.1 to 0.15% oxygen. The total concentration of other impurities (Si, Ca, Fe) does not exceed 0.1 to 0.2%.

13. PRODUCTION OF SOLID TUNGSTEN

As mentioned earlier, solid tungsten is prepared by powder metallurgy techniques, which were developed for the first time in 1826 by Sobolevskii for the production of platinum ware. The method comprises the following stages:

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1) pressing of powder (into bricks, bars);
2) sintering (heating to a given temperature);
3) working into the final product (by forging, drawing or rolling).

Pressing

When the powder is pressed, the product is an aggregate of a certain shape and possesses a certain mechanical strength. The mechanical strength increases because the particles have been brought close together and the contact area between them has increased, which results in an increase in the cohesive forces (which are inversely proportional to the distance between the particles) and in the mechanical binding forces between the particles.

The freely-flowing powder possesses a certain strength since its particles are in contact with each other although the contact area is quite small. The strength of the freely-flowing powder is characterized by the angle of repose α, the larger the angle of repose, the higher the strength of the powder. Fine powders have a large surface area; hence, the cohesive force in such powders is higher than in coarse powders; this is displayed as a larger value of the angle of repose and a lower bulk density of the powder.

The cohesion and mechanical binding forces of the powder interefere with its compaction since a certain effort must be exerted in order to overcome these forces. Hence, powders with a lower bulk density are compressed with more difficulty.

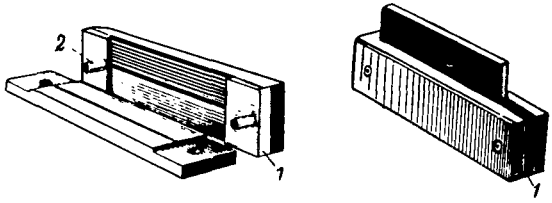

FIGURE 20. Dies for pressing tungsten powder into bars.
1—face plates; 2—joint pins.

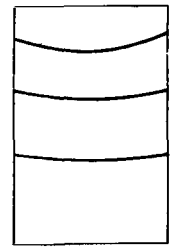

FIGURE 21. The distribution of powder layers in a pressed briquette.

Powders with a nonuniform particle size usually have a higher bulk density and produce denser pressed compacts than powders of uniform particle size. However, the selection of the optimum particle size of the powder is not governed by compressibility alone. The effect of the particle size on processes occurring during sintering must also be taken into account.

The pressing of tungsten powder into bars is carried out in detachable steel dies (Figure 20).

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The pressure exerted upon the powder during pressing is not uniformly distributed within the compact. This is due to the friction between the powder particles and the walls of the die. As a result, in any vertical section through the compact, the upper layers (i.e., the layers lying nearer to the ram) are denser than the lower layers; in the upper layers the density increases from the center to the periphery, while in the lower layers it increases from the periphery to the center (Figure 21). The nonuniform pressing is exhibited especially strongly in the case of compacts of considerable height. Hence, the shape of the dies used in the pressing of tungsten powder must be such that the compression takes place along the smallest dimension.

A lubricating substance — a solution of glycerol in alcohol (in a ratio of 1.5 : 1) or of paraffin in gasoline (4 to 5% paraffin) — is also added to the powder before the pressing, in order to prevent stratification and to obtain a compact of uniform thickness. During pressing the lubricating solution is squeezed out onto the walls of the die and reduces the friction between the wall and the powder particles.

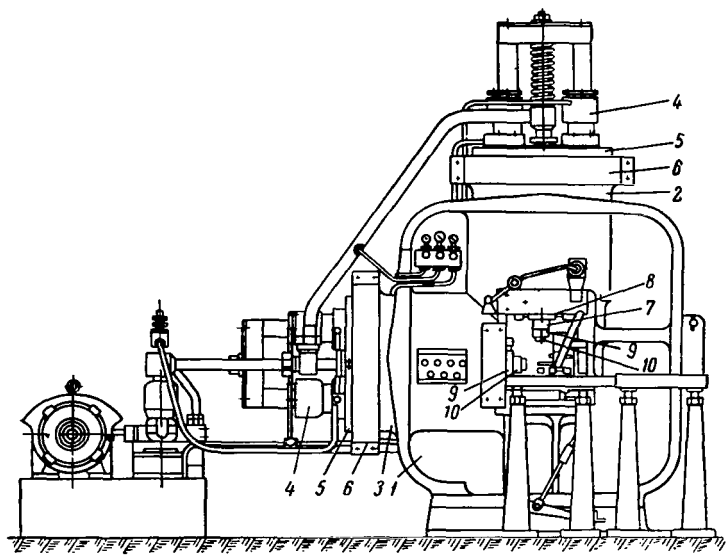

FIGURE 22. A 520-ton hydraulic press.

1—press bed; 2 and 3—vertical and horizontal cylinders; 4 and 5—cylinders serving to return cylinders 2 and 3 to the starting position; 6—rings joining the cover to the press bed; 7—piston rods; 8—directing wedge; 9—plunger; 10—replaceable gib (of the plunger).

The pressing of tungsten powder is carried out with hydraulic presses of 270 to 2000 tons. The press most commonly used in the Soviet plants is a 520-ton hydraulic press, P-801 model (Figure 22).

The pressed tungsten bars have a cross section of 10×10 to 40×40 mm, and a length of 500 to 650 mm. The pressure applied during pressing ranges from 2.5 to 5 tons/cm^2, depending on the nature of the powder and

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the size of the bar*. The density of the bars produced under those conditions is 12 to 13 g/cm^3, corresponding to a porosity of 30 to 40%. The porosity of the pressed tungsten bar cannot be reduced since the tungsten crystals have a very high strength in the cold and are not deformed during pressing. When the tungsten particles have been compacted to a degree such that their displacement ceases, any further increase in the pressure causes chipping or lamination of the bar, which under these conditions behaves as a compact body.

The limiting pressure (above which lamination takes place) is known as the critical pressure and its value for tungsten is 4 to 6 tons/cm^2.

Sintering

The sintering of tungsten bars is a two-stage process: the first stage is a low-temperature presintering intended to increase the strength and the electrical conductivity of the bar, while the second stage is high-temperature sintering.

Low-temperature presintering. The presintering is carried out at 1150 to 1300° in a hydrogen atmosphere. The bars remain in the hot zone of the furnace for 30 to 120 minutes (depending on the size of the bar). Occasionally, the presintering is carried out in two stages: first at 850 to 900° (this removes volatile substances such as glycerol, alcohol) and then at 1150 to 1300°.

The compressed bars have open porosity and therefore the hydrogen diffuses into the pores during sintering and reduces the thin oxide layers formed on the crystal surfaces. The reduction produces a true metallic contact between the crystals in the bar. The fine metallic crystals produced in the reduction of the oxide films are located between the larger primary tungsten crystals. They promote sintering of the particles because of their high surface activity.

Presintering results in a noticeable strengthening of the bars. These are subject to linear contraction which may be as high as 2 to 3% of the initial length.

Low-temperature sintering is carried out in electric tube or muffle furnaces (Figure 23). The muffle (or tube) of the furnace is made of alundum (Al_2O_3) which does not soften up to 1600°; a molybdenum-wire heater is used. In order to protect the molybdenum heater against oxidation, the furnace casing (which is insulated with chamotte bricks) is made gas-tight and hydrogen is supplied continuously through a nozzle in the furnace cover. Since the alundum is porous, the hydrogen passes

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* Hence, the minimum rated power of a press for the smallest bars would be:

$$\frac{10 \times 500 \times 2.5}{100} = 125 \text{ tons},$$

while for the largest bars it would be:

$$\frac{40 \times 650 \times 5}{100} = 1300 \text{ tons}.$$

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from the casing into the furnace space and mixes with the main stream of hydrogen which enters the furnace from the discharge end through the cooler of the furnace.

The pressed bars are mounted in nickel boats whose bottoms are covered with a thin layer of tungsten powder. Each boat contains from 3 to 30 bars, (depending on their size).

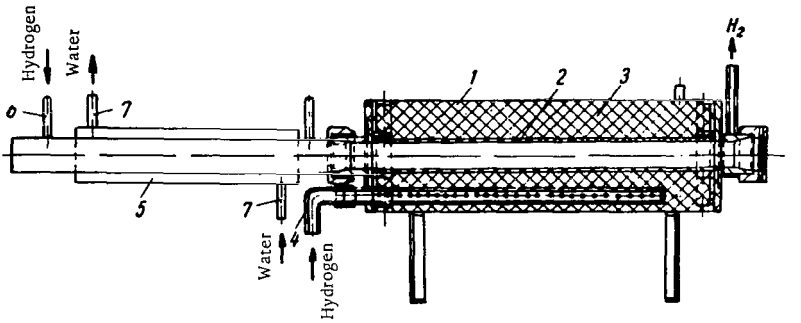

FIGURE 23. Muffle furnace used in bar sintering.

1—iron casing; 2—alundum tube with molybdenum heater; 3—thermal insulation (alundum powder packing); 4—hydrogen supply tube to the casing; 5—cooler; 6—tube for the supply of hydrogen to the furnace space; 7—water entry and outlet tubes.

High-temperature sintering. The preparation of massive metal having the most favorable structure for subsequent mechanical working requires that the bar be heated to about 3000° during the sintering. Such a high temperature is achieved by the direct passage of an electric current through the presintered bar. In practice, this operation is known as "welding" and is carried out in a special "welding" apparatus (Figure 24). The bar is clamped (in a vertical position) between two contacts consisting of copper blocks containing two tungsten plates connected by a spring to form a clamping device. The blocks have grooves for cold water circulation. The water-cooled copper tube which supplies current to the lower contact passes through an opening in a steel plate fitted with a circular groove. The groove contains a rubber ring which supports a water-cooled copper cap. During sintering, dry hydrogen is fed continuously from below the cap at a rate of 0.8 to 1.0 m^3/hr. The lower contact must be movable as a noticeable linear contraction of the bar takes place during sintering (the length of the bar is reduced by 15 to 17%) and firm clamping may result in destruction of the bar. The mobility of the lower contact is ensured by supplying the current by means of flexible busbars. A counterweight is used to tighten the bar.

The power needed for sintering the bar is dissipated mainly as radiation from the incandescent surface of the bar and the clamps. Only a small fraction of the heat (1 to 2%) is used in heating the bar. Hence, the maximum power required for sintering depends on the bar surface and the temperature.

The radiation intensity from a unit surface of the incandescent metal is proportional to the fourth power of the absolute temperature of its surface

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$$E = c\left[\frac{T}{100}\right]^4,$$

where E is the radiation intensity (watt/cm^2), and c is the Stefan-Boltzmann constant.

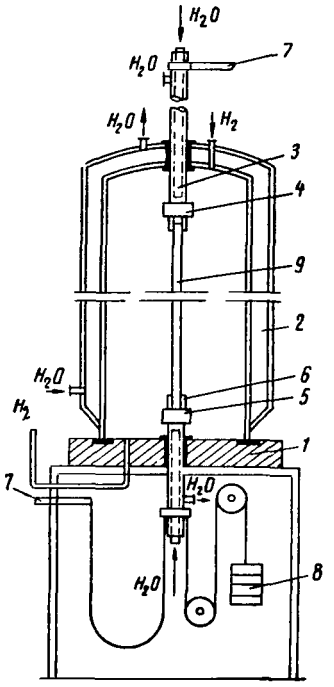

FIGURE 24. Apparatus for high-temperature bar sintering.

1 — steel plate; 2 — cover; 3 — busbar; 4 — upper stationary contact; 5 — lower movable contact; 6 — clamps; 7 — current-supply busbars; 8 — counterweight; 9 — tungsten bar.

The radiation intensity emitted by tungsten at various temperatures is shown on page 2. At a sintering temperature of 3030° (3300°K) the radiation intensity is 245 watt/cm^2. Making use of these data, it is possible to calculate the energy radiated by the entire surface of the bar (i. e., the approximate power required) by means of the equation:

$$W = S \cdot 245,$$

where W is the total radiation energy in watt and S is the incandescent surface area (cm^2).

For the smallest bar (10 × 10 × 500 mm) the required power would be

$$W = 1 \times 50 \times 4 \times 245 = 49\,000 \text{ watt} = 49 \text{ kw},$$

while for the largest bar it would be (40 × 40 × 650 mm)

$$W = 4 \times 65 \times 4 \times 245 = 254\,800 \text{ watt} = 254.8 \text{ kw}.$$

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These results are somewhat low since the energy radiated by the end surfaces of the bar and the tungsten plates holding the bar ends has been neglected. Moreover, a part of the heat is lost by convection through the hydrogen atmosphere. The various heat losses are tabulated in Table 12.

TABLE 12

Distribution of heat in the "fusion" of tungsten bars,%

Item (heat losses)	Bar size, mm	
	11 x 11 x 500	32 x 32 x 450
Heat lost through radiation from the bar surface	76.0	76.0
Heat lost through radiation from the bar ends	0.5	5.5
Heat lost through radiation from the holding clamps	13.0	8.0
Heat lost through hydrogen convection	0.5	0.5
Other losses	10.0	10.0

The external view of a group of sintering devices is shown in Figure 25.

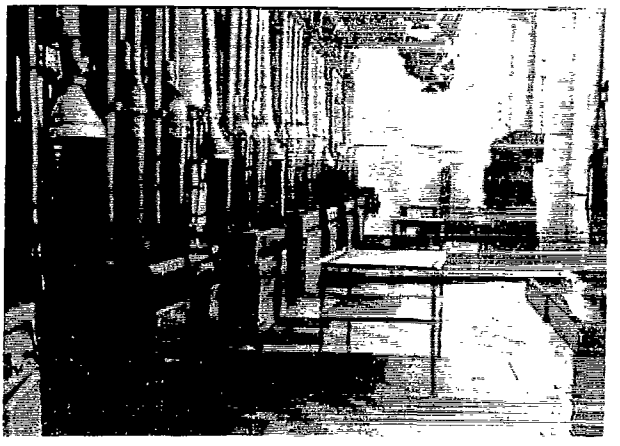

FIGURE 25. External view of a group of sintering furnaces.

Since the tungsten bar has a low electrical conductance (at a relatively large cross section — 1 cm^2 and up, and a length of 500 to 650 mm), it requires a large low-voltage current to heat it to 3000°. Thus, a current of 2500 amp is required for a bar with a cross section of 10 × 10 mm, while 10,000 to 12,000 amp is required for large bars. The voltage applied to the end of the bar is usually 10 to 20V.

Hence, the current is supplied to the sintering furnace through a step-down transformer, while an autotransformer (connected to the high-voltage side of the step-down transformer) is used for continuous adjustment of the current strength. The consumption of electrical energy may be reduced through the use of several thin cylindrical molybdenum screens which are placed concentrically round the bar. Such screens reflect a fraction of the radiated energy and reduce the consumption of electrical energy by about 20 to 30%. However, heat losses by convection through the hydrogen reduce the effectiveness of screening.

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The simultaneous sintering of several bars, which is a recent process, permits a noticeable reduction in the consumption of electric energy and increase in the output /30/. Six to eight bars are sintered simultaneously in one unit (Figure 26). The bars are placed in a single row. As a result, energy losses through radiation are lower than is the case with the same number of bars sintered separately since there is mutual screening of the inner surfaces of the bars. The current passes successively through all the bars, thus increasing the electrical resistance by a factor of 6 to 8 and permitting the use of lower currents and higher voltages for heating the bars to the sintering temperature.

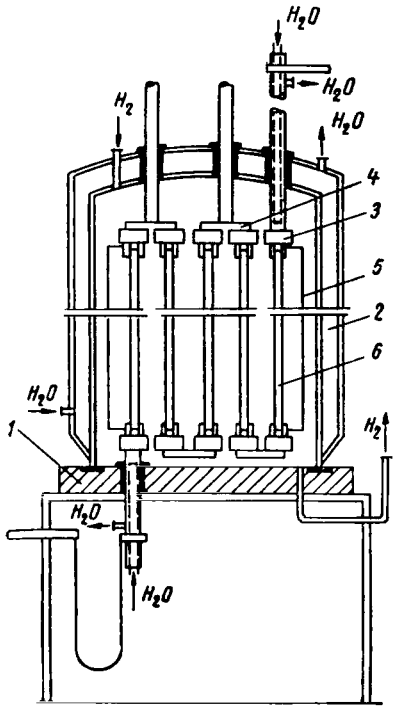

FIGURE 26. Sintering apparatus for a group of bars.

1—base; 2—cover; 3—contact heads; 4—connector; 5—molybdenum screen; 6—bars.

The bar temperature is determined by the current intensity, which is proportional to the power supplied. Hence, at a constant resistance of the bars (constant size and powder structure) the sintering conditions are established and controlled by adjusting the current intensity. Accordingly, one or two sample bars are used to find the current required to fuse the bar (the fusion current) before the sintering of a group of bars is carried out. The bar is fastened between the contacts, the cover is set in place, a hydrogen atmosphere is produced, and the current is increased continuously until fusion of the bar occurs.

Sintering conditions for the whole group of bars are thus established. During sintering, the current is increased within 8 to 10 minutes to the maximum value, i.e., to 88 to 95% of the fusion current. The current is maintained at the maximum level for 12 to 15 minutes, and is then switched off. The cover is removed 4 to 5 minutes after the interruption of the current, and the bars are taken out*.

The bar contracts during sintering, and its density increases from 12 to 17.5 to 18.5 g/cm^3. The residual porosity is 10 to 15%. The external appearance of pressed and sintered bars is seen in Figure 27.

A recent practice is to use automatic control instruments, which are programmed to adjust the intensity of the current passing through the bar /3/. Such control yields homogeneous bars and makes for better working efficiency.

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* In the case of some brands of tungsten sintering is carried out in two stages. In the first stage the current is increased to 40 to 50% of the fusion current and is maintained at that level for 5 to 7 minutes. This produces vaporization of most of the additives (see p. 56) which are then deposited on the inner parts of the apparatus. The second stage of sintering is carried out in another vessel.

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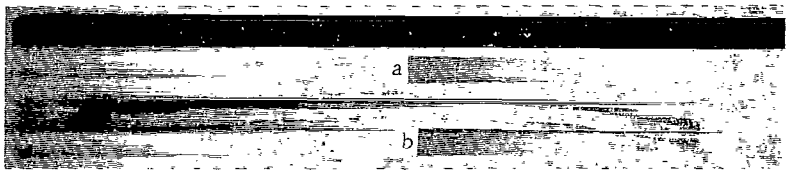

FIGURE 27. Tungsten bars.

a—compressed; b—sintered.

Sintering mechanism /7/

The sintered tungsten has the polyhedral structure characteristic of compact metals (Figure 28). However, in contrast to the metal prepared by melting, the tungsten prepared by sintering still possesses some porosity which is eliminated only through mechanical working of the bar (forging, drawing).

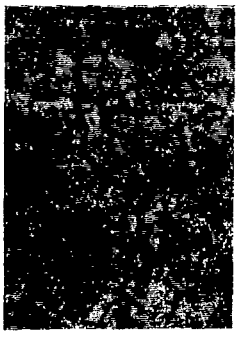

FIGURE 28. Structure of a sintered tungsten bar.

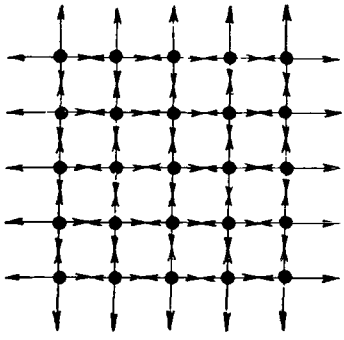

FIGURE 29. Degree of saturation of atomic force fields in crystals.

The processes of contraction and particle growth taking place during sintering are associated with the increased mobility of atoms at the sintering temperature. It is well known that the atoms in the crystal lattice of a solid have a certain vibration amplitude which increases with increasing temperature. In contrast to the atoms inside the crystals, the atoms on its surface have unsaturated force fields (Figure 29), which results in an excess of free energy which is exhibited as surface tension and tends to reduce the free area of the crystals.

As the temperature is increased, there is an increase in the mobility of surface atoms which move (migrate) from lattice points (less stable sites) into cavities and particle-contact points at which the excess of free energy is less. The atomic configuration thus becomes more stable. The surface migration of the atoms results in an increased smoothness of the free surfaces and spheroidization of the pores. The total area of contact between the particles increases, as is evident from Figure 30.

However, the surface migration of atoms cannot be the cause of the contraction of the sintered bars, since the total pore volume remains the same.

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The contraction is caused by surface tension which tends to reduce the total free surface in the sintered bar. The particles are deformed and "flow" into the pores. Such deformation is made possible by the fact that when the temperature is increased, the strength of the crystals decreases more rapidly than does the surface tension.

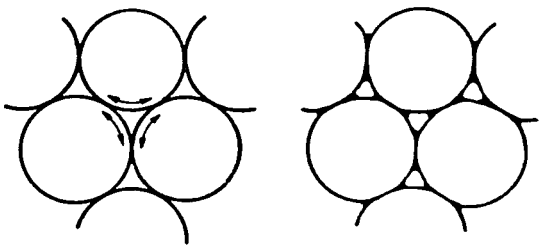

FIGURE 30. The increase in contact areas and the spheroidization of pores as a result of the surface migration of atoms.

a—before sintering; b—after sintering.

Recrystallization (growth of some particles at the expense of others), which begins at a given temperature, promotes rapid movement of the atoms and activates the forces of surface tension causing the contraction. Noticeable contraction usually also takes place during sintering at temperatures below the crystallization temperature. It is associated with the volume deformation of the particles which has been mentioned above.

Structure of the bars

The sintered bars should have a fine-grained uniform structure. The formation of such structure depends on several factors: temperature changes during sintering, grain size of the initial tungsten powder, and the presence of small amounts of special additives (SiO_2, K_2O, Na_2O, ThO_2, Al_2O_3, etc.).

During high-temperature sintering, the tungsten bar is heated in a non-uniform manner. There is a temperature drop between the center and the periphery, as well as between the middle of the bar and its ends. The bar surface is cooled by heat radiation, while the bar ends are at a lower temperature, being in contact with the cool clamping device. The temperature difference may cause a faster growth of the crystals. The structure of the bar may be controlled by changing the rate of heating: a bar with a fine-grained structure is obtained by a rapid increase of the temperature in the range of accelerated crystal growth (2600 to 2800°). The structure of the bar is also affected by the grain size of the initial powder. Coarse powders with an average particle size of 8 to 10 μ are not suitable for the production of compact metal, and neither are powders which are too fine. The latter have a more pronounced tendency towards grain growth than the coarse powders. Powders with a particle size of 0.5 to 5 to 6 μ (average particle size = 2 to 3 μ) are used for the production of metal with a fine-grained uniform structure.

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The best workability during the subsequent hot-forging operation is obtained in the case of sintered tungsten bars with a uniform structure and an average grain size of about 22 μ (i. e., 2000 grains per mm^2).

The typical structure of a bar sintered at a high temperature is shown in Figure 28.

In order to control the recrystallization taking place in incandescent tungsten wires used in electric lamps and electronic devices, and in order to obtain wires with a predetermined structure, a small amount of an additive, thorium oxide, aluminum oxide, or a silica-containing mixture ($SiO_2+Na_2O+K_2O$) is added to the tungsten intended for use in wire manufacturing. The additives are usually added as a solution of the respective salts to a suspension of tungstic acid in water. The components are thoroughly mixed, the mixture is evaporated, dried, and forwarded to the reduction stage. The composition of the additive and the amount of it introduced into the tungsten determine the brand of the finished product.

Most of the silica and the alkali metal oxides are vaporized during sintering and entrain with them other admixtures (CaO, MgO, etc.). This cleanses the surfaces of the separate crystals (the admixtures are present as films on the intercrystalline boundaries) and thus promote the rapid sintering and increase in density of the bars.

The thorium and aluminum oxides are not expelled during sintering and affect the structure of the sintered bar, depending on the amount added. As a rule, thorium oxide at concentrations of 0.75 to 1.1% interferes with crystal growth during sintering.

Quality control of the sintered bars

The parameters checked in the quality control of the bars are: external appearance, physical properties, chemical composition, and microstructure.

The bars must have a uniform, somewhat lustrous surface, and must not absorb ink lines traced on their surface. This is an indication of the required porosity. The curvature deflection must not exceed 4 mm for a bar length of 300 mm. The difference between the thicknesses of the ends must not exceed 0.7 mm, and the difference between the lengths of the bar faces (over its cross section) must not exceed 0.4 mm. The bars must contain at least 99.8% W, and the maximum permissible impurity contents in % are:

Ln_2O_3	0.02
Ni	0.005
CaO	0.015
SiO_2	0.01
Mo	0.04

The density of the bars, as measured by hydrostatic weighing on a technical balance, must be within 17.5 to 18.5 g/cm^3.

As mentioned above, the bar must have a uniform structure, which is controlled by examination under the microscope. The number of grains per mm^2 must be between 800 and 2000, corresponding to an average grain size of 35 to 22 μ.

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In addition, the quality of a tungsten bar is determined by its workability; to test this, 7 or 10 sample bars are taken out of each batch and subjected to all stages of mechanical working.

Mechanical working of sintered bars

The sintered tungsten bars are brittle and cannot be forged at room temperature. They have a very low tensile strength and their elongation is virtually zero.

In contrast to the usual behavior of other metals, fine-grained crystalline tungsten bars (10,000 to 12,000 grains/mm^2) are more brittle than coarse-grained bars (1000 to 5000 grains/mm^2).

At high temperatures the bars may be forged and then drawn. If subjected to gradual deformation, with intermediate annealing periods, their ductility increases. Ultimately, wires with a diameter of 0.01 to 0.015 mm may be drawn.

The changes in tungsten structure brought about by mechanical working are shown in Figure 31. The polyhedral structure becomes fibrous.

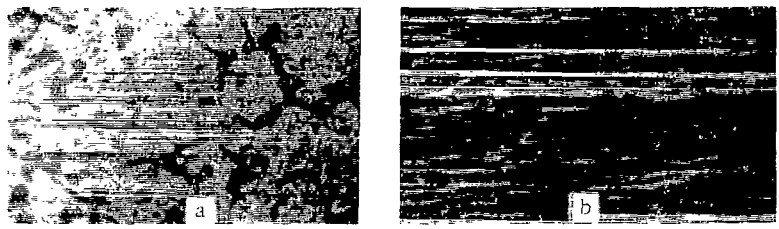

FIGURE 31. Changes in the structure of a tungsten bar as a result of forging.

a—sintered bar; b—forged rod, 2 mm in diameter.

Forging is carried out on a special rotational forging machine (Figure 32). The heated bar is subjected to a large number of strokes (10,000 to 12,000 per minute) by two forging dies which rotate very rapidly around the tungsten rod as axis. The forging machine consists of a cast-iron stationary base 1; the base carried rollers 3 mounted so as to form a circle. A shaft 2 rotates in the space between the rollers; the shaft has a central channel to accommodate the bar and a groove containing two loosely held forging dies. As the shaft is rotated, the dies move in alternation from the center to the periphery by centrifugal force and from the periphery to the center (by the projecting roller) striking the bar. The working part of the forging dies has grooves whose size corresponds to the diameter of the rod being worked. The number of strokes per minute depends on the number of rollers and the rotational velocity of the shaft: at a velocity of 1000 rpm with 10 rollers the number of strokes is 10,000 per minute. The dies are made of fast-cutting steel.

Before forging, the bars are heated in a molybdenum-coil furnace, in a hydrogen atmosphere. As the diameter of the rod decreases, the forging

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temperature is reduced from 1350 to 1200°. In forging from a diameter of 9 to a diameter of 5 mm, the bars are manually fed to the forging machine. When the diameter is reduced the bars are fed to the next machine in which the dies have a smaller diameter. In the next forging stage (reduction of the diameter from 5 to 2 mm) the rods are fed mechanically to the forging machine by means of a special conveyor. The rod first passes through a gas-heated furnace in which its temperature is increased to 1300° (Figure 33). In order to prevent oxidation and to reduce wear of the dies, the rod is preliminarily coated with a layer of aquadag (a mixture of fine graphite and ammonia water containing sugar).

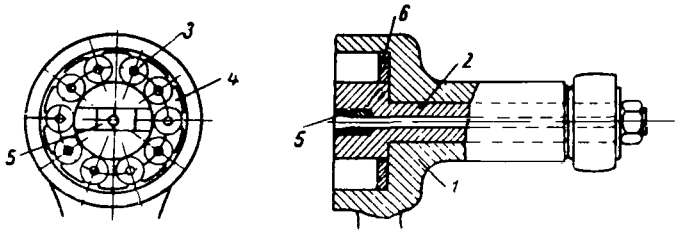

FIGURE 32. Design of a rotational forging machine.

1—base; 2—forging ram; 3—rollers; 4—steel ring; 5—forging dies; 6—steel rings to clamp the [large] ring.

The hot bars are drawn first on large drawing machines fitted with hard-alloy draw plates (here the diameter is reduced from 2 to 0.5 mm) and then on medium and fine-drawing machines (from 0.5 to 0.01 mm). Diamond dies are used for drawing wires thinner than 0.3 mm.

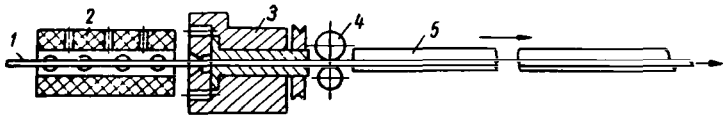

FIGURE 33. Positioning of installation in the forging of tungsten.

1—bar to be forged; 2—furnace; 3—forging machine; 4—transporting device; 5—guiding table.

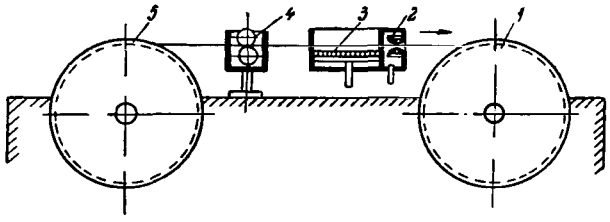

FIGURE 34. Setup for the drawing of tungsten wire.

1—guiding drum; 2—draw plates; 3—gas furnace; 4—lubricating box; 5—release drum.

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The drawing of tungsten wire is schematically shown in Figure 34. The wire passes successively through a lubricating box containing aquadag, and then through a gas furnace where it is heated. It is then squeezed through the hot drawing plates and is wound on the guiding drum. Depending on the wire diameter, the drawing temperature varies from 800 to 550°.

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Chapter II

MOLYBDENUM

14. GENERAL DATA ON MOLYBDENUM

Brief historical note

The term molybdenum comes from the Greek word "molybdos". Up to the eighteenth century the term molybdenum was used to designate lead, galena, many lead-like minerals and graphite.

The most common molybdenum mineral, molybdenite, was for many centuries believed to be a modification of graphite, which it resembles in appearance.

The element molybdenum was discovered in 1778 by the Swedish chemist Scheele. He isolated molybdic acid by decomposing molybdenite with nitric acid and he prepared a number of molybdic acid salts.

Metallic molybdenum was obtained for the first time in 1781 by Hjelm, a compatriot of Scheele, by reducing molybdenum trioxide with carbon. The metal, in a purer form, was prepared at the beginning of the nineteenth century by Berzelius, who used hydrogen as the reducing agent.

At the end of the nineteenth century it was found that addition of molybdenum imparts to steel a high strength and a capacity for self-quenching. Extensive production of molybdenum steels began in 1910, the year in which it was found that molybdenum imparts special properties to gun steels. Later molybdenum became a most important alloying element in various steels.

Commercial production of metallic molybdenum and its use in electrical technology began at about the same time as the production of tungsten in 1909 to 1910 when a powder-metallurgy method was developed for the production of those metals in a solid form.

Properties of molybdenum

The physical, mechanical, and chemical properties of molybdenum resemble those of tungsten, but there are certain differences.

The physical properties of molybdenum are listed below.

Atomic number	42
Atomic weight	95.95
Density, g/cm^3	10.2

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Lattice type and parameter	Body-centered cubic $a = 3.14$ Å
Melting point, °C	2620 ± 10
Boiling point, °C	~ 4800
Superconductivity transition temperature, °K	0.9 to 0.98
Heat of fusion, cal/g	50
Heat of sublimation, cal/g	1620
Heat capacity, cal/g, °C (20 to 100°)	0.065
Heat conductivity, cal/cm·sec, °C (at 20°)	0.35
Coefficient of [thermal] expansion (25 to 700°)	5.8 to $6.2 \cdot 10^{-6}$
Resistivity, ohm·cm·10^6 at temperatures (°C):	
20	5.17
730	23.9
1330	41.1
1730	53.1
Radiation intensity, watt/cm^2 at temperatures (°C):	
730	0.55
1330	6.3
1730	19.2
2330	70
Electron work function, eV	4.37
Thermal neutron capture cross section, barns	2.6
Brinell hardness, kg/mm^2:	
sintered bar	150 to 160
2 mm sheet	240 to 250
annealed wire	140 to 185
Tensile strength of wire, kg/mm^2:	
unannealed (depending on the diameter)	140 to 260
annealed (elongation 20 to 25%)	80 to 120
Modulus of elasticity of wire, kg/mm^2	28,500 to 30,000

Molybdenum is one of the highest melting metals. Only tungsten, rhenium, and tantalum have melting points higher than molybdenum. Noteworthy physical properties of molybdenum are its high boiling point and electrical conductance (which is lower than that of copper but higher than that of iron or nickel) and its relatively low linear expansion coefficient (about 30% of that of copper). The hardness and the tensile strength of molybdenum are lower than those of tungsten. Molybdenum is readily worked under pressure. The mechanical properties are strongly affected by the degree of purity of the metal and its mechanical and thermal history.

One of the important properties of molybdenum is its low thermal neutron capture cross section (about one seventh of that of tungsten), which permits its use as a structural material in atomic reactors.

Molybdenum is stable in air at ambient temperatures. Slight oxidation (to an irridescent color) is observed at 400°. The metal is rapidly oxidized above 600°, with the formation of MoO_3. Above 700° molybdenum is rapidly oxidized by steam to the dioxide, MoO_2:

$$Mo + 2H_2O \rightleftarrows MoO_2 + 2H_2.$$

Hydrogen does not react with molybdenum up to the melting point of the metal. However, some gas is absorbed, with the formation of a solid

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solution, when the metal is heated in a hydrogen atmosphere. At 1000° the solubility of hydrogen is 0.5 cm^3 per 100 g of the metal.

Molybdenum reacts with nitrogen at temperatures above 1500° with formation of the nitride. At low nitrogen pressures ($\sim$ 0.01 mm Hg) no such reaction is observed up to 2400°.

The metal interacts with solid carbon, hydrocarbons, and carbon monoxide at 1100 to 1200° with the formation of the carbide Mo_2C.

Fluorine attacks the metal at ambient temperatures, while chlorine attacks it above 250° when the volatile halides, MoF_6 and $MoCl_5$ respectively, are formed. Iodine vapor does not react with molybdenum. Molybdenum reacts with bromine at high temperatures.

Molybdenum disulfide, MoS_2, is formed in the reaction of molybdenum with sulfur vapor above 440° or with hydrogen sulfide above 800°. Sulfur dioxide oxidizes the metal at 700 to 800°.

Silicon reacts with molybdenum above 1200°. The disilicide $MoSO_2$ formed is very stable in the air up to 1500°.

Molybdenum is resistant to hydrochloric and sulfuric acids at room temperature, but dissolves to a certain extent in these acids at 80 to 100°.

Molybdenum is dissolved slowly by nitric acid or aqua regia in the cold, and rapidly at elevated temperatures.

Molybdenum is not attacked by hydrofluoric acid, but dissolves rapidly in a mixture of nitric and hydrofluoric acids. A mixture of five volumes of nitric acid, three volumes of sulfuric acid, and two volumes of water is a useful solvent for molybdenum.

Molybdenum is not attacked by cold solutions of alkali hydroxides. Some etching takes place in hot solutions. The metal is rapidly oxidized by fused alkalies, especially in the presence of oxidants, with formation of molybdates.

The properties of molybdenum compounds

Molybdenum belongs to group VIB of the periodic table. Its most common valency is six. Its most important compounds are molybdenum trioxide, molybdic acid, and the molybdic acid salts, molybdates. There are also compounds of bi-, tri-, tetra-, and pentavalent molybdenum.

Oxides. Molybdenum forms a series of oxides of which the trioxide MoO_3 and the dioxide MoO_2 are the most stable. There are also some intermediate oxides, including a relatively stable oxide, Mo_4O_{11}.

Molybdenum trioxide MoO_3 is formed in the oxidation of molybdenum or its lower oxides, and in the roasting of the mineral molybdenite, MoS_2.

Molybdic anhydride is a white powder with a faint greenish hue. Upon heating MoO_3 assumes a bright-yellow color. The density of MoO_3 is 4.69. Its melting and boiling points are 795 and 1155° respectively.

At 800 to 1000° molybdenum trioxide vapor exists as the associate $(MoO_3)_3$ /23/.

Noticeable vaporization of molybdenum trioxide takes place above 600 to 650° (see Table 16). The heat of formation of MoO_3 is 178 ± 1.5 kcal/mole.

Hydrogen at 800 to 900° reduces molybdenum trioxide to the metal.

The approximate solubility of MoO_3 in water at 20° is 0.4 to 2 g/l. The resulting solution is acidic (pH = 4 to 4.5).

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Molybdenum trioxide dissolves in hydrochloric and sulfuric acids. MoO_3 dissolves in aqueous alkalies and ammonia, with formation of molybdates.

Molybdenum dioxide MoO_2 is a dark-brown powder produced by reducing MoO_3 with hydrogen at 450 to 470°. Its density is 6.34 and its heat of formation is 141 kcal/mole.

Molybdenum dioxide is virtually insoluble in water, aqueous solutions of alkali hydroxides and non-oxidizing acids. Nitric acid oxidizes MoO_2 to MoO_3.

The intermediate oxide Mo_4O_{11} is formed by reduction of MoO_3 with hydrogen, by careful oxidation of MoO_2, and by heating a mixture of MoO_3 and MoO_2 or MoO_3 and molybdenum powder in an inert atmosphere (e.g., in nitrogen). Mo_4O_{11} has a blue-violet color.

The oxide is sparingly soluble in water, sulfuric and hydrochloric acids and dilute solutions of alkali hydroxides.

Molybdic acid and molybdates. White voluminous precipitates of hydrated molybdenum trioxide are formed when molybdate solutions are treated with acids. The dihydrate $MoO_3 \cdot 2H_2O$ (or $H_2MoO_4 \cdot H_2O$) is stable up to 61°; the monohydrate $MoO_3 \cdot H_2O$ (or H_2MoO_4) is stable between 61 and 120°. Elimination of water, with formation of MoO_3, takes place above 120°. Molybdic acid is sparingly soluble in water, its solubility at 15 and 80° being 2.126 and 5.185 g/l respectively. It is, however, readily soluble in strong inorganic acids.

Molybdic acid salts are known as normal molybdates. Their composition corresponds to the formula $Me_2O \cdot MoO_3$ or Me_2MoO_4, where Me_2O is a monovalent metal oxide.

Molybdic acid can add on various numbers of MoO_3 molecules with formation of polyacids whose composition corresponds to the general formula $xH_2O \cdot yMoO_3$, where $y > x$. The salts of these acids are known as polymolybdates. In contrast with the normal molybdates, the Me_2O: MoO_3 ratio in the polymolybdates is smaller than unity and varies over a wide range. Thus, for instance, the following types of molybdates are known:

$Me_2O \cdot 2MoO_3$ — dimolybdates

$3Me_2O \cdot 7MoO_3$, $5Me_2O \cdot 12MoO_3$ — paramolybdates

$Me_2O \cdot 3MoO_3$, $Me_2O \cdot 4MoO_3$ — metamolybdates

$Me_2O \cdot 10MoO_3$ — decamolybdates and many others.

Polymolybdates are formed in the neutralization of a solution of an alkali metal molybdate, or when MoO_3 is dissolved in a molybdate solution. Solutions at pH $\geqslant$ 6.5 contain only molybdate anions (MoO_4^{2-}). Polymerization with the formation of polyanions ($Mo_4O_{13}^{2-}$, $Mo_6O_{20}^{4-}$, and others) takes place in the pH range between $\sim$ 6.5 and 2.5. Cations (e.g., MoO_2^{2+} and more complex ones) are formed at pH below 2.5, and at pH below 1 the cations become the predominant form.

The normal alkali molybdates are readily luble in water; the molybdates of the alkaline earth metals, of lead, iron, copper, zinc, and other metals are sparingly soluble in water.

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The properties of some molybdates and polymolybdates are reviewed below.

Normal sodium molybdate Na_2MoO_4. This salt crystalizes from solutions in which the $Na_2O : MoO_3$ ratio is higher than unity. The dihydrate, $Na_2MoO_4 \cdot 2H_2O$, is formed between 10 and 100°, while the decahydrate is formed below 10°. The melting point of anhydrous Na_2MoO_4 is 627°, its density is 3.28.

The solubility of sodium molybdate in water at 15.5 and 100° is 39.27 and 45.57% respectively.

Sodium paramolybdate, $5Na_2O \cdot 12MoO_3 \cdot 38H_2O$, crystallizes from solutions of the normal sodium molybdate when these are neutralized to pH ≈ 5. The solubility of the crystalline hydrate at 30° is 157 g per 100 g water. The anhydrous salt is sparingly soluble in water.

Ammonium paramolybdate $3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O$ crystallizes out from ammoniacal solutions in which the molecular ratio $NH_3 : MoO_3$ is 6 : 7 or slightly higher. This ratio is produced by evaporation of the solution, the ammonia being expelled, or by neutralizing part of the ammonia.

Ammonium paramolybdate is stable in air. Its aqueous solutions are slightly acid. Its solubility in water at 20° is about 300 and at 80 to 90° about 500 g/l.

Ammonium paramolybdate begins to decompose at 150° with evolution of ammonia and formation of the tetramolybdate $(NH_4)_2O \cdot 4MoO_3$. The ammonia is expelled quantitatively at 350° and molybdenum trioxide remains behind.

Ammonium paramolybdate is a common commercial product and an intermediate in the production of pure molybdenum trioxide.

Calcium molybdate, $CaMoO_4$, occurs in nature as the mineral powellite. The salt is white. It is prepared from aqueous solutions of molybdates by the addition of calcium chloride. Calcium molybdate may be prepared by direct interaction of calcium oxide and molybdic anhydride at temperatures above 450°. The density of the salt is 4.28. Its melting point is 1520°.

The solubility of calcium molybdate in water at 20 and 100° is 0.0058 and 0.0235 g/100 g solution respectively /25/.

Calcium molybdate is an important technological product, used as an additive in steel. It is also used in the smelting of ferromolybdenum.

Iron molybdates. The normal ferrimolybdate, $Fe_2(MoO_4)_3 \cdot nH_2O$ separates out as a yellow precipitate when ferric chloride or sulfate is added to a solution of sodium molybdate. Precipitates, whose composition corresponds to the above formula, are formed only within a certain pH range (pH ≈ 3.5). The precipitate formed at higher pH contains iron hydroxide and has a brown color, while the precipitate formed at lower pH contains molybdic acid. When heated above 600°, the ferrimolybdate decomposes to yield Fe_2O_3 and MoO_3.

Ferrous molybdate, $FeMoO_4$, is not precipitated from molybdate solutions, since Fe^{2+} ions reduce $(MoO_4)^{2-}$ ions. However, $FeMoO_4$ is formed when a mixture of FeO and MoO_3 is heated at 500 to 600° in the absence of air.

Lead molybdate, $PbMoO_4$, is a white, sparingly soluble salt. It occurs in nature as the mineral wulfenite. The salt may be prepared

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by precipitation from solutions of alkali metal molybdates, or by heating a mixture of PbO and MoO_3 at 500 to 600°. The density of lead molybdate is 6.92. Its melting point is 1065°.

Copper molybdate. The anhydrous copper molybdate, $CuMoO_4$, is a green-yellow powder which is prepared by heating a mixture of CuO and MoO_3 at 500 to 700°. The salt melts with decomposition at 820°. The basic, bright-green copper molybdates are precipitated from aqueous solutions of sodium molybdate by the addition of copper salts. Depending on the conditions of precipitation, the composition of the precipitate either corresponds to the formula $CuO \cdot 3CuMoO_4 \cdot 5H_2O$ or resembles the composition of the mineral lindgrenite, $2CuMoO_4 \cdot Cu(OH)_2$.

Heteropolyacids and their salts. Molybdenum, like tungsten, has a tendency to form complex compounds with phosphoric, arsenic, silicic, and boric acids (see p. 6).

Ammonium phosphomolybdate — $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O$ or $(NH_4)_3H_4[P(Mo_2O_7)_6 \cdot 4H_2O$ — is one of the well known salts belonging to this type of compounds. It is a sparingly soluble salt which is precipitated when a solution of ammonium molybdate in nitric acid is poured into a phosphate solution containing HNO_3. This reaction is used extensively for the detection and determination of phosphoric acid.

Molybdenum blue. When a solution of molybdic acid or an acid molybdate solution is treated with a reducing agent such as SO_2, H_2S, Zn, glucose, etc., the solution assumes a deep-blue color which is associated with the formation of the so-called molybdenum blue. Molybdenum blue is a compound whose composition corresponds approximately to the formula $Mo_5O_{14} \cdot xH_2O$ (or according to other data — $Mo_8O_{23} \cdot x\,H_2O$). The composition is variable.

In solution molybdenum blue exists in a colloidal state and is readily adsorbed by surface-active substances, e. g., by plant or animal tissues, to which it imparts a blue color.

The formation of molybdenum blue is a widely used analytical reaction.

Molybdenum sulfides. Molybdenum forms four sulfides: MoS_3, Mo_2S_5, MoS_2, and Mo_2S_3. Only MoS_2 and MoS_3 are of industrial importance.

MoS_2 exists in nature as the mineral molybdenite, the main source of molybdenum (see p. 69). Synthetic molybdenum disulfide is produced by heating a higher sulfide in the absence of air, by the action of sulfur vapor on molybdenum powder or by fusing molybdenum trioxide with soda and sulfur.

The higher sulfide, MoS_3, is precipitated when H_2S is passed through hot acidified solutions of molybdates. Molybdenum trisulfide dissolves in ammonium and sodium sulfide solutions, with the formation of thiomolybdates:

$$MoS_3 + (NH_4)_2S = (NH_4)_2MoS_4.$$

The thiomolybdates are readily soluble in water. When their solution is acidified, they decompose with separation of molybdenum trisulfide:

$$(NH_4)_2MoS_4 + H_2SO_4 \rightarrow MoS_3 + (NH_4)_2SO_4 + H_2S.$$

The precipitation of molybdenum trisulfide is used in analytical chemistry for the determination of molybdenum and in industry for the extraction of molybdenum from solutions.

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TABLE 13

Some properties of molybdenum chlorides and oxychlorides /19/

Compound	Color	Behavior at various temperatures	Heat of formation, kcal/mole
$MoCl_5$	Violet-black	Melts at 194, boils at 268°. In the gaseous phase dissociates with formation of $MoCl_4$ (gas)	126.5
$MoCl_4$	Brown	The solid decomposes above 130° into $MoCl_3$ (solid) and $MoCl_5$ (gas). Between 330 and 1630° it is the main component of the gaseous phase	114.6
$MoCl_3$	Red-brown	The solid decomposes above 530° into $MoCl_2$ (solid) and $MoCl_4$ (gas)	94.0
$MoCl_2$	Yellow	The solid decomposes above 730° into molybdenum and $MoCl_4$ (gas)	69 0
MoO_2Cl_2	Yellowish-white	Melts at 170° at a pressure of 1.5 atm. At 156° the vapor pressure of the solid oxychloride is 1 atm.	173.0
$MoOCl_4$	Green	Melts at 104, boils at ~ 180°	153.5

Molybdenum chlorides. Molybdenum forms a number of chlorides and oxychlorides. The properties of some of them are shown in Table 13.

Molybdenum pentachloride is formed when the metal or the disulfide, MoS_2, is treated with chlorine above 500°. The lower chlorides may be prepared by reduction of $MoCl_5$ with hydrogen, or by thermal dissociation of the chloride. $MoCl_5$ hydrolyzes in humid air and in water with the formation of the oxychlorides, MoO_2Cl_2 and $MoOCl_3$.

Chlorine reacts with MoO_3 above 500° with formation of the volatile oxychloride, MoO_2Cl_2. This oxychloride may also be prepared by heating a mixture of MoO_3 and NaCl at 500 to 600° /11/.

Uses of molybdenum

Ferrous metallurgy. More than 75% of the total production of molybdenum is used in ferrous metallurgy for the production of alloy steels.

Molybdenum forms a solid solution in steel. The solubility of molybdenum in iron is ~ 8%. A fraction of the molybdenum exists as complex iron-molybdenum carbide.

Usually, molybdenum is introduced into the steel together with other alloying additives such as chromium, nickel, and vanadium; the molybdenum concentration in structural steels does not exceed 0.5%, while in high-speed steel in which it replaces tungsten its concentration reaches 7.5 to 8.5%.

Molybdenum noticeably improves the properties of steel by producing a uniform and fine-grained structure. By reducing the eutectoid decomposition temperature of steel, molybdenum widens the temperature range of hardening and tempering and affects the hardenability of steel. Molybdenum improves the following mechanical properties of steel: the elastic limit, the wear resistance, and the impact strength. Alloying

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of molybdenum with chromium-nickel steels eliminates tempering brittleness. This is one of the most valuable properties of molybdenum.

Molybdenum is usually added to steels in the form of ferromolybdenum (50 to 70% Mo). Calcium molybdate, which is cheaper than ferromolybdenum, is the form used when it is only necessary to introduce small amounts of molybdenum. During smelting the calcium molybdate is reduced by the iron. The molybdenum formed dissolves in the steel while the calcium oxide remains in the slag.

Molybdenum is also used in alloys of cast iron. Molybdenum reduces the grain size of gray iron and improves its high-temperature properties and wear resistance. Cast iron containing silicon and molybdenum is used for the production of acid-resistant equipment.

Heat- and acid-resistant alloys. Molybdenum is a component of many acid-resistant and heat-resistant alloys, the other components being mainly nickel, cobalt, and chromium.

The major components of heat-resistant alloys are nickel and cobalt, their concentration being as high as 50 to 60% . Most of the heat-resistant alloys, which are also acid-resistant, contain 20 to 30% Cr and 1 to 7% Mo. Alloys having maximum resistance to acids (i. e., which resist the effect of all mineral acids except hydrofluoric) contain up to 15 to 20% molybdenum. The other components are nickel, cobalt, chromium, and iron.

Molybdenum and molybdenum-base alloys. The high melting point, high-temperature strength, and high electrical conductivity of molybdenum are the reasons for its extensive use in the electrical bulb and radio industries. Molybdenum wire is used in the manufacture of filament supports in electrical bulbs and grids for electronic tubes. Molybdenum rods sealed into special glass are used as current terminals in electrical vacuum equipment.

Molybdenum is readily rolled into thin foils (0.1 to 0.2 mm thick) which are used in the manufacture of anodes for oscillator tubes and kenotrons. Molybdenum foil is also used in the manufacture of X-ray tubes.

Molybdenum wire and bands are used as heaters for high-temperature electric furnaces.

Molybdenum and tungsten wires are joined in thermocouples used for measuring temperatures from 1200 to 2000° in inert or reducing atmospheres.

The recently achieved production of large molybdenum ingots, weighing 1000 kg or more, has extended the possible uses of molybdenum. Molybdenum is now used either pure or as an alloy to ensure the maintenance of high-temperature strength, e. g., in the manufacture of turbine blades and other parts of jet engines and rockets.

In order to prevent high-temperature oxidation of molybdenum parts, they are coated with molybdenum silicide, a nickel-chromium alloy, or some other protective coating.

Molybdenum may be used as a structural material in nuclear power plants since it combines high-temperature strength with relatively small thermal-neutron capture cross section.

Large molybdenum rods (1 m long and 30 to 40 mm in diameter) have been lately used as heating elements in glass-melting furnaces. Molybdenum is virtually unaffected by molten glass. Molybdenum is also used in the manufacture of stirrers and other parts for glass-producing equipment.

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Uses of molybdenum compounds. Molybdenum disulfide (either pure molybdenite or synthetic MoS_2) may be used as a lubricant. Molybdenite lubricants are superior to graphite and may be used between -45 and +400°.

Sodium molybdate is extensively used in the manufacture of pigments and lacquers. Molybdenum compounds are used for dyeing silk, wool, cotton fabrics, and furs; advantage is taken of the fact that molybdates are readily reduced with formation of molybdenum blue.

The molybdenum oxides MoO_3 and MoO_2 are used as catalysts in the chemical industry.

The fact that microamounts of molybdenum in the soil stimulate growth in vegetables, especially the leguminous species, has been recently discovered. This has resulted in an extended use of molybdenum compounds (mainly ammonium molybdate) as fertilizers.

15. MINERALS, ORES, AND ORE CONCENTRATES

Molybdenum minerals

There are about twenty known molybdenum minerals, of which only four are of industrial value: molybdenite MoS_2, powellite $CaMoO_4$, molybdite $Fe_2(MoO_4)_3 \cdot 7\frac{1}{2} H_2O$ and wulfenite $PbMoO_4$.

Except for molybdenite, all these are secondary minerals formed in the weathering of the primary mineral — molybdenite.

Dispersed molybdenum is present as an impurity in limonite and in some sulfide minerals, mainly chalcopyrite.

Molybdenite MoS_2 is the most common and industrially most important molybdenum mineral. Molybdenite is a soft mineral with a metallic luster and a lead-gray color. In appearance it resembles graphite. The density of MoS_2 is 4.7 to 4.8, its Mohs hardness is 1 to 1.5.

The mineral has a hexagonal lattice with a lamellar structure (Figure 35). The molybdenum layers lie between two layers of sulfur ions, forming three-layer-packages. The structure of molybdenite satisfactorily explains the perfect cleavage of its crystals. It is due to the weak bonds between the three-layer S — Mo — S strata. Partial dissociation of molybdenite takes place upon heating to 1300 to 1350° in the absence of air. Molybdenite melts with decomposition at 1650 to 1700°. It is readily oxidized to MoO_3 when heated in air at 500 to 600°. Molybdenite is oxidized by nitric acid and aqua regia.

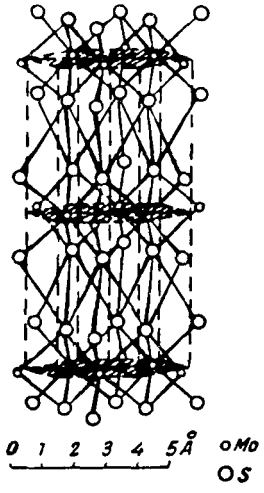

FIGURE 35. The crystal lattice of molybdenite.

Molybdenum is most often found in quartz veins, and is frequently associated with scheelite, wolframite, cassiterite, pyrite FeS_2, chalcopyrite $CuFeS_2$, arsenopyrite FeAsS, bismuthinite Bi_2S_3 and other minerals. Molybdenite often contains dispersed rare metal rhenium (an isomorphous impurity, in concentrations of 0.0001 to 0.04%).

The upper strata of molybdenite veins are oxidized as a result of weathering with the formation of molybdenum ochers, molybdite, powellite and wulfenite.

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Powellite, $CaMoO_4$, a product of oxidation of molybdenite, is frequently found as a secondary mineral in the form of a thin coating on molybdenite; it is rarely found as a primary mineral. The color of powellite ranges from white to gray, its density is 4.35 to 4.52; and its Mohs hardness is 3.5. The mineral often contains some tungsten since powellite and scheelite are isomorphous.

Molybdite $Fe_2(MoO_4)_3 \cdot 7\frac{1}{2}H_2O$ is formed in the weathering of molybdenite and is frequently found together with the latter in molybdenite oxidation zones. Molybdite has a variable composition, which is sometimes described by the general formula $xFe_2O_3 \cdot yMoO_3 \cdot zH_2O$. Molybdite may be an important source of molybdenum. For instance, about 25% of the molybdenum in the upper zones of the largest deposits outside the Soviet Union (in Climax, Colorado) is in the form of molybdite.

Wulfenite, $PbMoO_4$, is found in the oxidation zones of lead ore deposits. Depending on the concentration of impurities, the color of the mineral may be yellow, bright-red, olive-green, or grayish. Its density is 6.7 to 7.0, its Mohs hardness is 2.5 to 3.

This mineral is not of industrial importance at present.

Molybdenum ores and ore deposits

Molybdenum is one of the less common elements. Its average concentration in the Earth's crust is about 0.001%. The molybdenum concentration in ores is quite small. It is extracted from ores containing a few tenths or even a few hundredths of one percent of molybdenum.

There are several types of molybdenum ores:

1. simple quartz-molybdenum ores, in which molybdenite is found in quartz veins;
2. quartz-molybdenum-tungsten ores, which contain both molybdenite and wolframite;
3. skarn ores, in which molybdenite (often together with scheelite and some sulfides such as pyrite and chalcopyrite) is found in quartz veins which fill cracks in skarns (siliceous limestones);
4. copper-molybdenum ores in which molybdenite is associated with copper and iron sulfides. Some ores have a very low copper content, but in others copper is predominant and the molybdenum content is very small (a few hundredths or a few thousandths of one percent). However, the total reserves of molybdenum in these ores are large and they are an important source of the metal.

The largest molybdenum ore deposits outside the USSR are found in the western USA, Mexico, Chile, southeast Canada, southern Norway, and the eastern states of Australia. The yearly production of molybdenum in the western countries is 27,000 to 30,000 tons of the metal (as concentrates).

The Soviet Union has numerous molybdenum ore deposits which yield enough molybdenum to satisfy the needs of the industry.

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Concentration of molybdenum ores

Molybdenum-containing ores are concentrated almost exclusively by flotation, which results in a fully satisfactory separation of molybdenite from the gangue and the accompanying minerals. Gravitational concentration has limited use. Magnetic concentration is occasionally used as an additional operation for the separation of iron.

Molybdenite is an easily floated mineral. The simple quartz-molybdenum ores can be readily concentrated. Ores containing a few tenths or a few hundredths of one percent of molybdenite yield concentrates containing 85 to 95% MoS_2. The degree of extraction is 90%.

Usually, the first stage involves the collective flotation of sulfides. The molybdenite is then floated, using sodium sulfide or sodium or potassium cyanide in an alkaline medium (pH 8 to 8.4) as a depressor for the copper and iron sulfides. Standard molybdenite concentrate is obtained after several purification stages. Pine oil is used as the frothing agent, and kerosene, transformer oil, etc. are used as the collectors.

In the concentration of copper-molybdenum sulfide ores, the first product is a mixed copper-molybdenum concentrate. Different methods are used to separate the molybdenum from the copper:

a) flotation of the molybdenite while the copper sulfide is depressed by sodium sulfide or sodium or potassium cyanide;

b) flotation of the copper sulfide, while the molybdenite is depressed by starch.

A combination of gravitational methods (for the production of wolframite concentrates) and flotation (for the production of molybdenite concentrate) is used to concentrate quartz-tungsten-molybdenum ores.

In the concentration of skarn scheelite-molybdenite ores, the molybdenite is extracted first by flotation and the scheelite is then separated (by flotation, using fatty acids and water glass) from the tailings of the first flotation. Powellite accompanies the scheelite in the scheelite concentrate.

Concentration of the oxidized molybdenum minerals, powellite and molybdite, involves great difficulties. Methods have recently been developed for the processing of powellite ores, but the problem of concentrating molybdite-containing ores has not yet been solved.

TABLE 14

Technological requirements for molybdenite concentrates

Brand	Molybdenum concentration, minimum, %	Maximum impurity contents, %				
		P	As	Cu	SiO_2	Sn
KM1	50	0.07	0.07	0.5	5.0	0.07
KM2	48	0.07	0.07	1.0	7.0	0.07
KM3	47	0.15	0.07	2.0	9.0	0.07

The concentration of some copper-molybdenum and, especially, oxidized ores yields low-grade (with respect to molybdenum) concentrates, which are subsequently treated by hydrometallurgical methods to yield a "synthetic concentrate".

The technological requirements for molybdenite concentrates produced in the USSR are listed in Table 14.

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16. PROCESSING OF STANDARD MOLYBDENITE CONCENTRATES

Molybdenite concentrates are the primary raw material for the production of ferromolybdenum and molybdenum compounds of various degrees of purity, molybdenum trioxide, ammonium paramolybdate, sodium molybdate, and calcium molybdate.

Irrespective of the ultimate product into which the molybdate concentrate is to be converted, the first industrial operation to which the concentrate is subjected is roasting which yields a calcine consisting of molybdenum trioxide contaminated with a number of impurities. The calcines are used for the smelting of ferromolybdenum or for the production of pure molybdenum compounds, the most important of which is molybdenum trioxide. It is prepared either by volatilization or by hydrometallurgical (chemical) processing of the calcine.

Molybdenite concentrates may be processed directly by hydrometallurgical methods, omitting the preliminary roasting. Such methods include: treatment with nitric acid /2/, oxidation of molybdenite in alkaline solution by oxygen under pressure /21/, treatment of the concentrate with an alkaline solution of sodium hypochlorite /22/. These processes are under investigation.

17. OXIDATIVE ROASTING OF MOLYBDENITE CONCENTRATES

A number of chemical reactions are involved in the roasting of molybdenite concentrates. These reactions may be divided into four groups /18/:

1) oxidation of molybdenite with the formation of molybdenum trioxide;
2) interaction between molybdenum trioxide and molybdenite;
3) oxidation of the sulfide minerals of the accompanying elements (copper, iron, etc.) with formation of molybdates.
4) reaction between molybdenum trioxide and the oxygenated compounds of the admixtures (oxides, sulfates, carbonates) with the formation of molybdates.

The conditions under which these reactions take place will be discussed below.

Oxidation of molybdenite. The mineral molybdenite is rapidly oxidized by atmospheric oxygen above 500°, yielding molybdenum trioxide in an exothermic reaction:

$$MoS_2 + 3^1/_2O_2 \rightarrow MoO_3 + 2SO_2 + 266 \text{ kcal}.$$

This reaction is virtually irreversible and occurs even at very low concentrations of oxygen in the gaseous phase.

During the oxidation the molybdenite particles are coated by a film of the trioxide formed. Hence, the reaction rate is determined by the structure of the oxide film since the oxygen and the SO_2 must diffuse through the film in opposite directions (see Figure 36). It has been experimentally shown that a dense oxide film is formed at 400°, and the rate of oxidation is determined by the rate of diffusion of the gases through the solid film. The oxide film formed at 550 to 600° is porous (friable) and does not interfere with the course of the reaction. The rate of oxidation of the mineral at 600° is about 0.009 mm/min /10/.

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The high exothermic effect accompanying the oxidation of molybdenite permits the roasting of molybdenite concentrates to be accomplished at the expense of the heat of reaction.

It is well known that sulfides undergo spontaneous oxidation at temperatures above their flash point. The data in Table 15 show that molybdenite has a relatively low flash point, close to the flash points of pyrite and chalcopyrite.

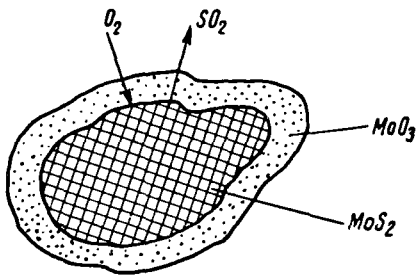

FIGURE 36. Oxidation of molybdenite particles.

TABLE 15

Flash point and heat of the oxidation reaction of some sulfides

Reaction	Heat of reaction, kcal/mole S_2	Flash point for a particle size < 0.063 mm, °C
$MoS_2 \rightarrow MoO_3$	266.3	365—465*
$2Cu_2S \rightarrow 4CuO$	253.8	465**
$2NiS \rightarrow 2NiO$	217.8	665
$2ZnS \rightarrow 2ZnO$	212.6	615
$FeS_2 \rightarrow 1/3\ Fe_3O_4$	189.2	360

* The first figure is for a particle size < 0.063 mm, the second for particle sizes between 0.09 and 0.127 mm

** For particle sizes of 0.09 to 0.127 mm.

Interaction between MoO_3 and MoS_2. In the absence of air (e.g., inside the particles formed as a result of overheating during roasting), the formation of molybdenum dioxide takes place (in the calcine) at 600 to 700°, through the reaction:

$$MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2.$$

As is evident from Figure 37, 45% of the MoS_2 in a mixture with MoO_3 reacts within 60 minutes (in an inert atmosphere at 600°), while at 700° about 90% of its reacts in the same time /11/.

Since MoO_2 is virtually insoluble in ammonia water, roasting must be carried out at temperatures not exceeding 600° in order to prevent sintering and interaction between MoS_2 and MoO_3.

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Oxidation of the sulfides of other metals. Roasting of molybdenite concentrates, carried out at 550 to 600°, causes the oxidation of iron, copper, and zinc sulfides which yield oxides (and partly sulfates) by the following reactions:

$$MeS + 1^1/_2O_2 \rightarrow MeO + SO_2;$$
$$2SO_2 + O_2 \rightleftarrows 2SO_3;$$
$$MeO + SO_3 \rightleftarrows MeSO_4.$$

It must be remembered that iron sulfates dissociate to a considerable extent above 450 to 500°, while copper sulfates dissociate above 600 to 650° and zinc sulfate reacted above 700°.

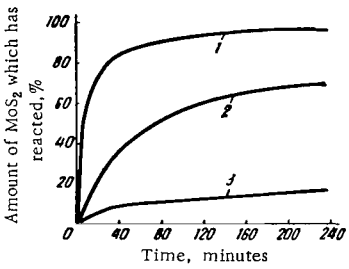

FIGURE 37. Rate of interaction of MoS_2 with MoO_3 at various temperatures.

1—700°; 2—600°; 3—500°.

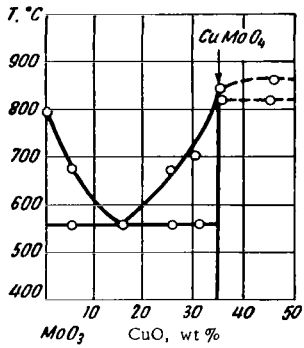

FIGURE 38. Phase diagram MoO_3 — CuO.

In addition to copper, iron, and zinc sulfates, calcium sulfate may also be formed during roasting if the concentrate contains calcium carbonate:

$$CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2.$$

Interaction of MoO_3 with oxide, carbonate and sulfate impurities. At 500 to 600° MoO_3 reacts with the oxides, carbonates and sulfates of a number of elements, yielding molybdates /11/:

$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2;$$
$$CuO + MoO_3 \rightarrow CuMoO_4;$$
$$CuSO_4 + MoO_3 \rightarrow CuMoO_4 + SO_3\,(SO_2,\ O_2);$$
$$ZnO + MoO_3 \rightarrow ZnMoO_4;$$
$$PbO + MoO_3 \rightarrow PbMoO_4.$$

The formation of $FeMoO_4$ may also take place in the absence of air. Upon heating in air, however, $FeMoO_4$ oxidizes and decomposes into Fe_2O_3 and MoO_3.

Copper molybdate and MoO_3 form a low-melting eutectic (560°, see Figure 38), which explains the lower sintering temperature of calcines

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with an increased copper content /18/. Of the above molybdates, those of calcium and lead are sparingly soluble in ammonia water. Their presence in the calcines causes a sharp decrease in the degree of extraction of molybdenum. Copper and zinc molybdates are readily soluble in ammonia solutions, while iron molybdate is slowly decomposed by ammonia water.

Molybdenite concentrates always contain silica. However, there is virtually no interaction between silica and MoO_3.

Roasting procedure

Until recently, the roasting of molybdenite concentrates was carried out in flame or muffle furnaces with manual raking of the material, in rotating tube furnaces and in multiple-hearth furnaces with mechanical raking.

The first two types of furnaces have serious drawbacks. They do not utilize the heat of the oxidation reaction; the roasting is carried out with a continuous supply of heat since there is no full countercurrent motion of the gases and the material being roasted. Moreover, temperature control in such furnaces is difficult. Overheating results in the sintering of the material, while the formation of lower molybdenum oxides and molybdates within the sintered particles reduces the degree of extraction of molybdenum from the calcine into the solution.

The multiple-hearth mechanical furnaces, in which the gas countercurrent penetrates all the material as it passes from one hearth to the other, are of more advanced design. As a result, there is better utilization of the heat and the roasting takes place mainly at the expense of the heat of reaction.

Fluidized-bed furnaces are used at present for the roasting of molybdenite concentrates in some plants in the USSR.

Roasting in multiple-hearth furnaces

Such furnaces have been used for a long time for the roasting of pyrites and of copper and zinc sulfide concentrates. These furnaces ensure good mixing, countercurrent flow of solid and gas, and rapid oxidation of the suspended material passing from one hearth to another.

A vertical cross section through an eight-hearth furnace, of which seven hearths are for roasting and the eighth, upper hearth is for drying, is shown in Figure 39. The furnace consists of a vertical cylinder made of steel sheets and lined with refractory (chamotte) bricks. The inner diameter of the furnace is 5.4m. The cylinder is divided into seven stories by refractory brick crowns, which also serve as the eight hearths. The distance between the centers of the hearths is 0.894 m. A rotating steel shaft, 1.29 to 1.52 m in diameter and lined on the outside with refractory bricks passes through the center of the furnace. The center shaft carries two rakes at each hearth, which are fastened to special

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sockets within the shaft. The rake is fitted with paddles, made of chromium-containing cast iron or a special alloy, to move the material. The center shaft and the rakes are air-cooled on the inside.

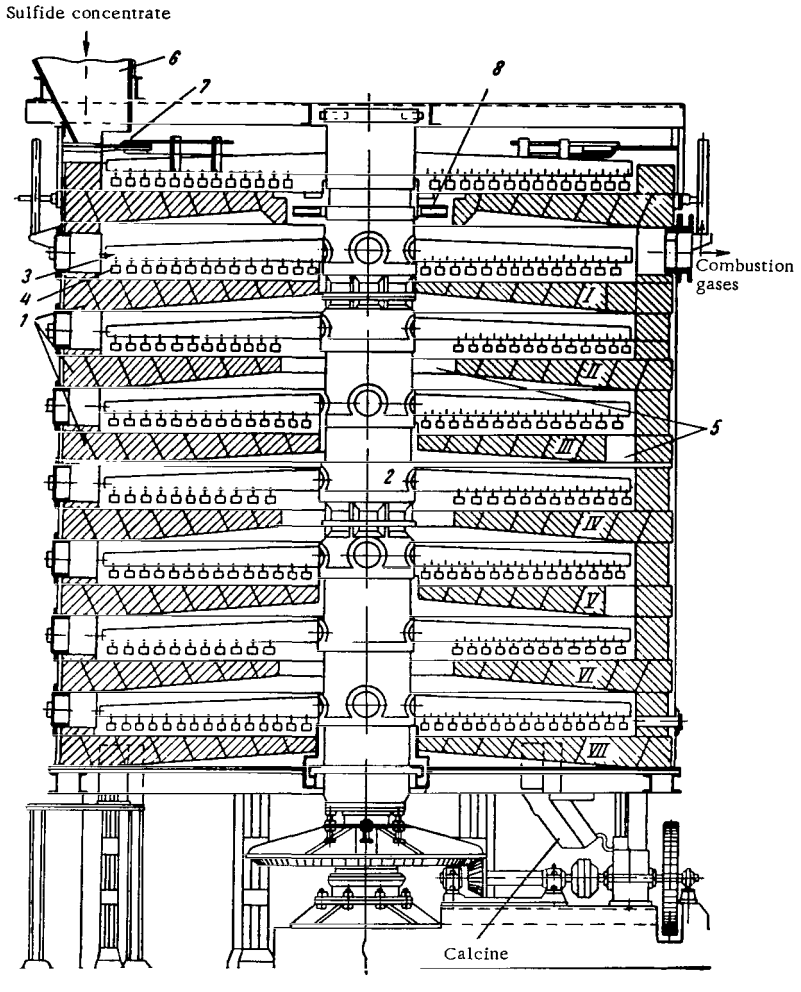

FIGURE 39. A mechanical multiple-hearth furnace.

1—crowns; 2—central shaft; 3—raker; 4—paddles; 5—openings in the crowns, for the passage of material; 6—storage bin for the concentrate; 7—feeder; 8—feed tray.

At the periphery or at the center of each hearth there are openings for the passage of solids and gases. The openings in the first, third, fifth and seventh hearths are made in the periphery, while in the remaining hearths they are made in the shaft. Such an arrangement

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ensures that the material passes through the entire surface of the hearths. Since the paddles over each hearth are placed at opposite angles with respect to the shaft, the material moves first from the periphery to the center and then from the center to the periphery and thus drops from hearth to hearth.

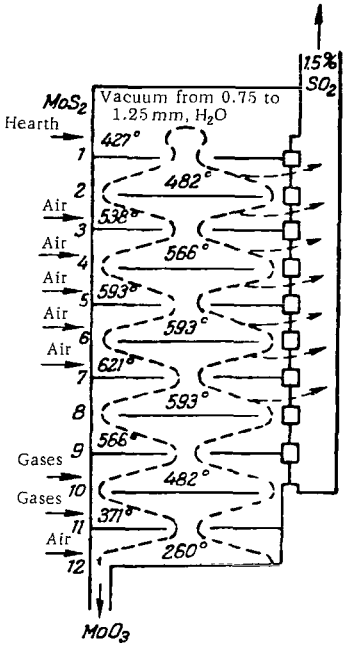

FIGURE 40. Temperature distribution on the hearths of a multiple-hearth mechanical furnace for the roasting of molybdenite. The air is introduced at each hearth and gases are led out through a common gas vent.

In order to ensure quantitative combustion of the sulfur, the lower hearths are fitted with burners. In addition, some of the hearths (e.g., the even-numbered ones) are fitted with burners to preheat the furnace. These burners are extinguished when the furnace becomes sufficiently hot. The hearth temperature must not exceed 600°. Temperatures as high as 750 to 800° must be avoided — MoO_3 melts at such temperatures, with consequent clogging of the openings and a rapid wear of the paddles — even though it is difficult to maintain the temperature at 580 to 600° in furnaces of this type.

The output of the furnace is 60 to 80 kg of concentrate per m^2 of hearth surface per day, depending on the operating conditions.

The dust entrainment with the exhaust gases reaches 8 to 10%. The SO_2 content in the gases is 3 to 5%.

In the Climax plant in the USA roasting is carried out in 8, 12, and 16-hearth furnaces. The temperature is controlled by a separate supply of air to each hearth. The gases pass out from separate outlets at each

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hearth to a common gas vent. This permits the maintenance of the required temperature at each hearth. The resulting temperature distribution in the hearths is shown in Figure 40. The dust entrainment is as high as 18%, the dust being mostly unroasted concentrate. The dust is trapped and returned for roasting in the furnace.

Fluidized-bed roasting

During the last 10 to 12 years the roasting of sulfide concentrates in chemical and metallurgical industries has also been carried out by processes in which the particles of the material are supported by an upward flow of gas in a "boiling" or pseudo-fluid state. The granular material reaches such state at certain gas velocities. The particle bed remains stationary at low gas velocities (below a certain critical value) (see Figure 41). As the critical velocity (v_{min}) is reached, the bed begins to expand and the material then passes into the "fluidized" state, which is characterized by a rapid motion of the particles in the gas stream, and the appearance of the bed resembles that of a boiling liquid. As the gas velocity is increased further to a new critical value (v_{max}), the whole bed becomes fluidized and is entrained with the gas stream.

The advantages of fluidized-bed roasting are associated with the following properties of such beds.

1. Good contact is ensured between the particles and the gas, so that chemical reactions in a fluidized bed take place at a high rate.

2. The mobility of the layer (which resembles the mobility of a liquid) permits an easy, continuous gravity discharge ("efflux") of the material from the furnace through the discharge tube.

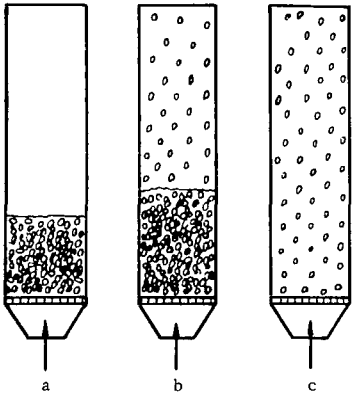

FIGURE 41. The three states of granulated material in an upward stream of gas.

a—stationary (filtering) bed; b—fluidized bed; c—suspended state.

3. Fluidized beds are characterized by a high thermal conductivity and high heat-transfer coefficients. This permits the required temperature to be maintained throughout the volume of the bed, even when the heat of reaction is high. The removal of excess heat from the bed is easily accomplished with the aid of coolers (for instance, water-cooled tubes fitted inside the bed).

The chemical nature of the roasting of molybdenite concentrates discussed above shows that in order to produce calcines with a high content of extractable molybdenum it is necessary that the roasting be carried out at closely controlled temperatures in order to avoid sintering. The contact between the particles must also be kept to a minimum in order to eliminate, as far as possible, formation of molybdates. These conditions are best satisfied during fluidized-bed roasting.

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The fluidized-bed roasting of molybdenite concentrates was first studied in the USSR. It is now used on an industrial scale /12/.

The design of one industrial furnace and of the whole installation are shown in Figure 42. The furnace consists of a refractory chamber with a rectangular cross section, whose lower part is fitted with an air-distributing screen. The screen consists of a series of steel nozzles with mushroom-shaped removable caps (Figure 43). The space between the nozzles is filled with heat-resistant concrete. The air inlet holes are beneath the mushroom-shaped caps. This prevents leakage of the solid material below the screen.

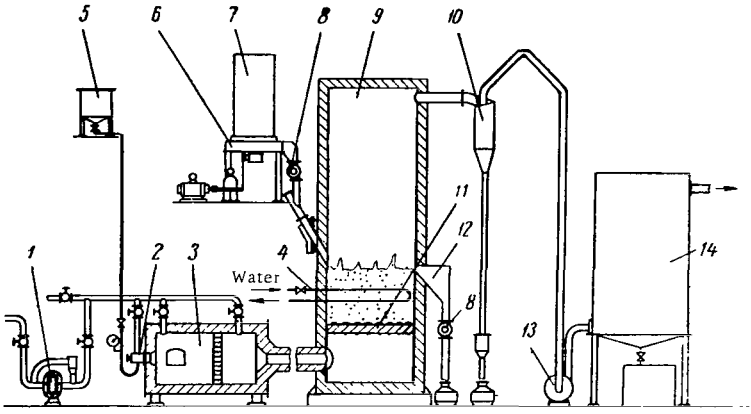

FIGURE 42. Fluidized-bed installation for roasting molybdenite concentrates.

1—air blower; 2—burner; 3—pressurized fire-box; 4—water-cooling system for the removal of excess heat; 5—fuel oil storage; 6—tray-type feeder; 7—bin; 8—gate valve; 9—furnace chamber; 10—cyclone; 11—screen (grate); 12—discharge baffle; 13—smoke exhaust; 14—electrostatic filter.

Uniform feeding rate of concentrate to the furnace is most important in maintaining the required roasting conditions. Nonuniform feeding of the concentrate causes sharp changes in the temperature of the bed, since the oxidation reaction is accompanied by the evolution of large amounts of heat. The feed of the concentrate to the furnace is controlled by an automatic feeding device which consists of a cylindrical bin (the concentrate "sticks" to a conical bin) and a tray-type feeder with an adjustable rotational velocity beneath the bin. The feeder blade moves the concentrate into the bin of a hermetically closed gate from which it flows by gravity through a spout into the fluidized bed.

At a height of 1000 to 1500 mm above the furnace hearth there is a discharge hole (discharge baffle) from which the calcine is discharged continuously and fed into the collectors through a gate valve.

The gases, together with the entrained fines, are let out through gas vents at the top of the furnace chamber. The gases pass through dust traps (cyclones, electrostatic filters) and are discharged into the atmosphere.

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The bed temperature is regulated automatically. The temperature control system is based on variations in the concentrate supply rate. When the temperature becomes too high or too low, as compared with the required temperature, there is an automatic decrease or increase of the rate of feed of the concentrate. This is accomplished by varying the rate of rotation of the feeder trays. Practice has shown that the system permits a reliable temperature control to within ±2.5° of the average preset temperature /13/.

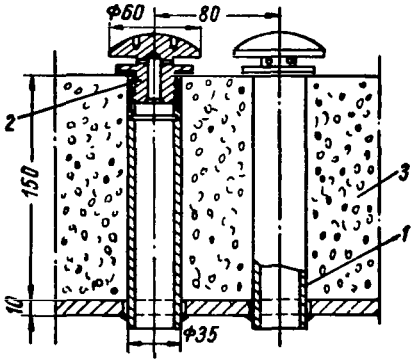

FIGURE 43. Design of a nozzle in the air distributing screen.

1—pipe; 2—removable cap with holes; 3—heat-resistant concrete.

If the average rate of feeding of the concentrate is such that too much heat is evolved, the excess heat is removed by water flowing through tubes accommodated inside the fluidized bed.

In order to start the operation of the furnace, calcines heated to the flash point of the molybdenite concentrate (500 to 510°) are fluidized by means of hot air, and the concentrate is then fed in (at a rate of about 50 to 60 kg/hr · m^2 of furnace hearth). As the concentrate falls onto the bed, it is ignited and the temperature increases. After 15 to 30 minutes it reaches the optimum roasting temperature of 560 to 570° which is then maintained by the automatic control system.

The height of the bed increases as more concentrate is fed in; continuous discharge of the calcines starts when the height reaches the discharge baffle.

A fraction of the concentrate fines (20 to 40%, depending on the granulometric composition of the concentrate) is entrained from the bed with the gases. Quantitative trapping of the dust is effected by a system of cyclones and an electrostatic filter (90 to 95% of the dust is trapped in the cyclones).

Under the roasting conditions described above, the dust is not quantitatively oxidized (the degree of oxidation is 70 to 85%) and it contains 8 to 10% sulfur. The dust may be returned to roasting after preliminary granulation (particle consolidation) in a ladle-type granulator.

Both furnace construction and roasting conditions are still being improved, but the experience already gained with the first industrial furnace models has shown that the process has some definite advantages:

a) the furnace output is 1200 to 1300 kg/m^2 of furnace hearth, which is 15 to 20 times higher than that of conventional roasting furnaces;

b) the process is completely automatic (the roasting takes place by the heat of reaction at closely controlled temperature);

c) the quality of the calcine produced (the content of extractable molybdenum) is higher than that of calcines produced in hearth furnaces; this is attributed to the suppression of reactions leading to the formation of molybdates and MoO_2.

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18. PRODUCTION OF PURE MOLYBDENUM TRIOXIDE

Distillation method

The vapor pressure of MoO_3 as a function of the temperature is shown in Table 16. Molybdic anhydride begins to volatilize below its melting point. However, a noticeable increase in the vapor pressure occurs only above the melting point (795°). Volatilization at an industrially useful rate takes place only at 900 to 1100°.

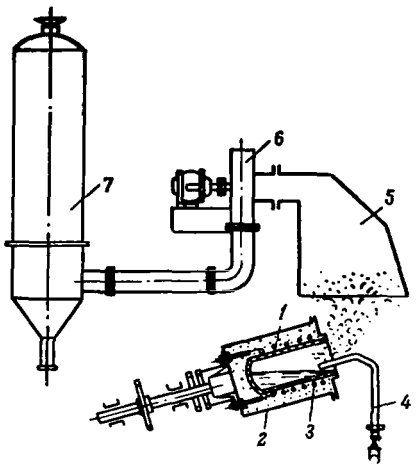

FIGURE 44. Distillation of molybdenum trioxide.

1—quartz crucible; 2—jacket; 3—electric heater; 4—compressed air supply; 5—exhaust hood; 6—fan; 7—bag filter.

In addition to MoO_3, *the calcines may* contain impurities such as molybdates and oxides of contaminant metals. Iron, copper, and silicon oxides are not volatilized at 900 to 1100°. Calcium molybdate is thermally stable up to 1200 to 1300° and is not volatilized. Copper molybdate, $CuMoO_4$, decomposes at 820° into CuO and MoO_3. Lead molybdate, $PbMoO_4$, volatilizes noticeably at its melting point (1050°). Hence, if lead molybdate is present the distillation must be carried out below 1000° *in order to prevent contamination* of the condensate with lead. There is practically no interaction between MoO_3 and quartz, and the volatilization of MoO_3 is not affected by the presence of quartz.

A diagram of one of the possible ways of carrying out the distillation is shown in Figure 44. The roasted molybdenite concentrate is placed in the quartz crucible of a rotating electrical furnace. The furnace has a slope of 35°. The sloping position of the furnace results in an increase in the surface of volatilization of the MoO_3. The crucible is heated to 900 to 1000° with the aid of an electric coil heater. At that temperature the calcines melt. Air is fed continuously to the crucible, and the air stream entrains the MoO_3 vapor. The trioxide vapor passes from the furnace into a bag filter through a hood, fitted over the furnace, and a fan system.

Distillation may also be carried out in a continuous-action furnace with a rotating hearth /24/.

Of the total amount of molybdenum in the initial calcine, 60 to 70% is thus volatilized. The remaining fraction is extracted from the residue by hydrometallurgical methods.

The trioxide produced by the distillation process contains 99.95% MoO_3. It is in a highly dispersed state (its bulk weight is 0.5 g/cm^3). Such "light" and bulky powders cannot be conveniently transported. Before packing, the molybdenum trioxide is moistened with a small amount of distilled water and is compressed and dried. This results in an increase in the bulk density to 3.5 g/cm^3.

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TABLE 16

Vapor pressure of MoO_3

Temperature, °C	Pressure mm Hg	Temperature, °C	Pressure mm Hg
600	0.000	850	23.4
610	0.009	900	53.9
625	0.018	950	105.1
650	0.05	1000	179.8
720	0.60	1050	288.3
750	1.75	1100	476.2
800	10.1	1155	760.0

Chemical methods /2, 3/

The ammoniacal method for the processing of calcines is diagrammatically shown in Figure 45. This is the most extensively used method. The calcines are leached with a solution of ammonia. The ammoniacal solution is treated to remove impurities and the molybdenum is isolated as ammonium paramolybdate or other polymolybdates (see below). Molybdenum trioxide is prepared by thermal decomposition of ammonium molybdate.

Leaching

On leaching with a solution of ammonia, molybdenum trioxide passes from the calcines into solution:

$$MoO_3 + 2NH_4OH = (NH_4)_2MoO_4 + H_2O.$$

The degree of extraction of the molybdenum depends on the composition of the calcine. In addition to MoO_3 the calcine may contain calcium, copper, zinc, and ferrous molybdate, MoO_2, non-oxidized molybdenite, copper and calcium sulfates, iron oxide, silica, alkali metal salts, tungsten minerals and other impurities.

Calcium molybdate, MoO_2, and molybdenite are virtually insoluble in ammonia solutions. The molybdenum in these compounds remains behind in the leaching tailings.

The copper, zinc, and nickel molybdates and sulfates are readily soluble in ammonia solutions, yielding ammoniates /26/.

$$MeMoO_4 + 6NH_4OH \rightarrow [Me(NH_3)_4](OH)_2 + (NH_4)_2MoO_4 + 4H_2O;$$
$$MeSO_4 + 6NH_4OH \rightarrow [Me(NH_3)_4](OH)_2 + (NH_4)_2SO_4 + 4H_2O.$$

Ferromolybdate is decomposed by ammonia solutions, but the reaction is slow because of the formation of the virtually insoluble ferric and ferrous hydroxides, which coat the molybdate particles /26/. A fraction of the ferrous iron is dissolved by the ammonia solution in the form of an ammoniate complex:

$$Fe(OH)_2 + 6NH_4OH \rightarrow [Fe(NH_3)_6](OH)_2 + 6H_2O.$$

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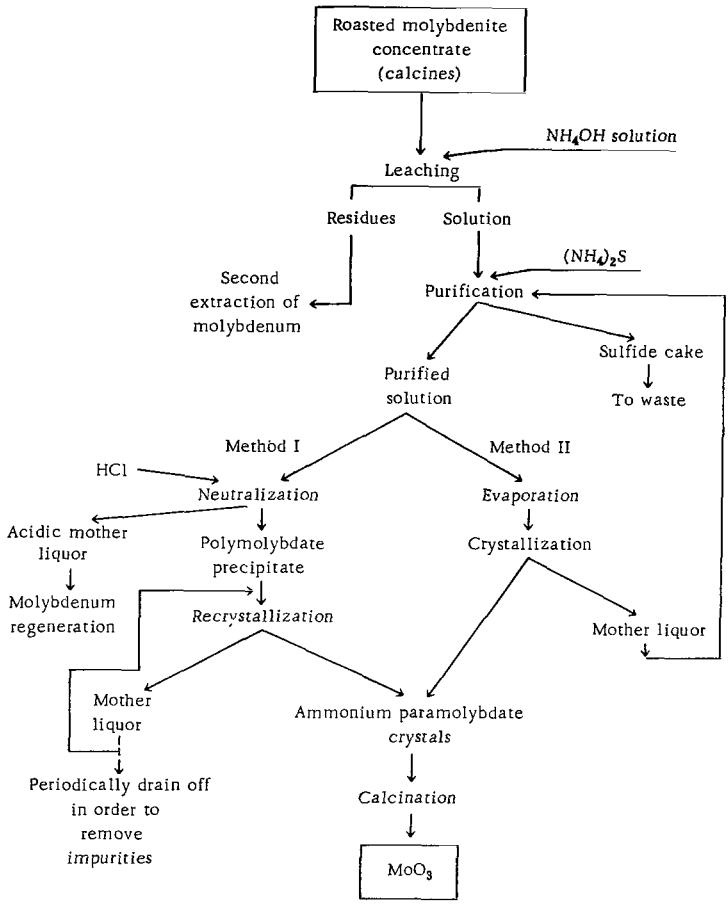

FIGURE 45. Production of pure molybdenum trioxide from molybdenum calcines.

Depending on the composition of the calcines, the degree of extraction of molybdenum into the ammoniacal solution ranges from 80 to 95%. The amount of residue [tailings] (i. e., the weight of the residues with respect to the weight of the initial calcines) ranges from 10 to 30%, and the molybdenum concentration in the residue ranges from 5 to 25%. As a rule, a second extraction of molybdenum from the residue is required.

In order to reduce the degree of extraction of impurities into ammoniacal solution, the calcines are occasionally washed with water before processing with ammonia solution. The water dissolves copper sulfate and alkali metal salts. However, it must be taken into account that some molybdenum is lost because of the higher solubility of MoO_3 in water in the presence of impurities /26/. The MoO_3 concentration in the aqueous solution is 3 to 5 g/l, and may occasionally be higher. The losses of molybdenum with the wash waters reach 4 to 5%.

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The calcines are leached with an 8 to 10% solution of ammonium hydroxide in the cold or at 70°; the leaching is carried out in iron vessels. Rotating-drum extractors or vats fitted with mechanical stirrers are used.

The drum extractors have the advantages of being hermetically sealed and of ensuring good mixing as well as the possibility, when filled with balls, of effecting additional grinding.

The stirrer-fitted extractors are not hermetically sealed. As a result, a part of the ammonia evaporates and the consumption of ammonia is increased. Depending on the type of apparatus used, the consumption of ammonia is 115 to 140% of the stoichiometric amount.

Three or four successive processing stages are used in order to provide a higher degree of leaching of molybdenum from the calcines. The solutions from the first two processing stages are collected together and are treated to remove impurities. The weak solutions from subsequent leachings are returned to the initial leaching stage. The slurries from each leaching stage are filtered on filter presses or suction filters. The residues are rinsed with hot water and the wash waters are recycled to the first leaching stage. The residue is subjected to a second molybdenum leaching stage (see p. 87).

The strong ammonia solutions from the leaching contain 140 to 190 g MoO_3/l. Their density is 1.10 to 1.16.

Removal of copper and iron from the solutions

The ammoniacal solutions are contaminated with copper, iron, occasionally zinc and nickel, alkali metal and sulfate ions.

Copper and iron are removed as sulfides by the addition of ammonium sulfide. Copper and iron sulfides are practically insoluble, the solubility of CuS being 9.1×10^{-23} moles/l. In spite of the fact that copper is bound as a stable complex, the solution always contains some copper ions whose amount corresponds to the equilibrium dissociation reaction:

$$[Cu(NH_3)_4]^{2+} \rightleftarrows Cu^{2+} + 4NH_3.$$

As the Cu^{2+} ions react to form the sulfide, the equilibrium continuously shifts until quantitative precipitation of the copper takes place:

$$[Cu(NH_3)_4](OH)_2 + NH_4HS + 3H_2O \rightarrow CuS + 5NH_4OH.$$

Iron sulfide is precipitated in the same way.

The amount of ammonium sulfide added must be closely controlled since an excess of it in solution leads to the formation of thiomolybdates which contaminate the ultimate product:

$$(NH_4)_2MoO_4 + 4NH_4HS \rightleftarrows (NH_4)_2MoS_4 + 4NH_4OH.$$

Ammonium sulfide solution is poured into the ammoniacal solution in small portions. An aliquot is taken after each addition and the degree of precipitation determined. The solution is then tested for sulfide ions by the addition of lead nitrate to a separate aliquot of the solution. A black precipitate (lead sulfide) is formed in the presence of an excess of

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ammonium sulfide, while a white precipitate (lead molybdate) forms in the absence of such an excess.

The excess ammonium sulfide is bound by the addition of a certain amount of fresh ammoniacal solution from the calcine-leaching operation.

The sulfides are precipitated in wood or rubber-lined iron vats with stirring.

Isolation of molybdenum from the ammoniacal solutions

Separation of ammonium paramolybdate by evaporation. The normal ammonium molybdate $(NH_4)_2MoO_4$ is stable only in solutions containing an excess of ammonia. A part of the ammonia is expelled during evaporation of the solution and ammonium paramolybdate is formed:

$$7(NH_4)_2MoO_4 + 4H_2O \rightarrow 3(NH_4)_2O \cdot 7MoO_3 + 8NH_4OH.$$

In order to prevent the formation of more acidic molybdates (of lower ammonia content), it is necessary that an excess of free ammonia (4 to 6 g/l) be maintained during the evaporation, and that the solution be stirred in order to prevent local overheating. Molybdates more acidic than the paramolybdate are precipitated as finely crystalline, sparingly soluble precipitates.

Solutions from which the heavy metals have been removed are taken for evaporation. These solutions contain 120 to 140 g MoO_3/l. Their density is 1.09 to 1.12. The solutions are evaporated in stainless-steel kettles fitted with jackets, in a two-stage process. Advance evaporation is carried out to a density of 1.20 to 1.23. The solution is allowed to stand and is filtered to remove the small amount of precipitate formed (copper and iron sulfides, as well as iron hydroxides which are precipitated as a result of the coagulation of finely-dispersed suspended particles). The main evaporation stage is then carried out and the density of the solution increases to 1.38 to 1.40, i.e., to a MoO_3 concentration of about 400 g/l. The hot solution is filtered and collected in crystallizers.

Crystallization is generally carried out in stainless steel crystallizers containing stirrers and a cooling system. A finely-crystalline precipitate consisting of ammonium paramolybdate $3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O$ separates out as the solution cools. The paramolybdate crystals are separated from the mother liquor by centrifuging, and are washed with cold distilled water directly in the centrifuge. The mother liquor is again evaporated and an additional amount of paramolybdate crystallizes out. Several successive crystallizations are carried out. About 50 to 60% of the salt present in the solution separates out during the first crystallization. The paramolybdate from the first two crystallization stages is of high purity. The residual mother liquor, which contains the concentrated impurities, is evaporated to dryness and the residue is ignited at 350 to 400°. The resulting contaminated MoO_3 is returned to the calcine-leaching stage.

This method of production of the paramolybdate has several disadvantages:

1) it is time-consuming, since it requires several successive evaporations and crystallizations;

2) the crystals from the second and subsequent crystallization stages often contain an increased amount of contaminants, above the technologically

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permissible concentration, so that it is necessary to carry out additional recrystallizations. For these reasons, the polymolybdate separation method is now extensively used in the Soviet Union.

Separation of polymolybdate by neutralization /14/ Polymolybdates of various compositions are precipitated during the neutralization of ammonium molybdate solutions by hydrochloric acid; their composition depends on the ultimate pH of the solution and the temperature.

In manufacturing practice, the precipitation is carried out from solutions containing 280 to 300 g MoO_3/l. When necessary, the solutions are preliminarily concentrated by evaporation.

Up to 96 to 97% of the molybdenum is contained in the precipitate in the form of tetramolybdate dihydrate if the hot (55 to 65°) solution is carefully neutralized with hydrochloric acid (to a pH between 2 and 3). The hydrolysis reaction is given by the equation:

$$4(NH_4)_2MoO_4 + 5H_2O \rightarrow (NH_4)_2O \cdot 4MoO_3 \cdot 2H_2O + 6NH_4OH.$$

The crystalline precipitate formed must be rapidly separated by filtration, since the dihydrate is converted into the anhydrous tetramolybdate $(NH_4)_2O \cdot 4MoO_3$ on prolonged contact with the mother liquor. The conversion is accompanied by a decrease in crystal size. A highly dispersed precipitate which is difficult to filter is formed as a result.

After centrifuging and washing with water, the polymolybdate precipitates still contain a small amount of contaminants. Most of the contaminants (Zn, Cu, Ni, Sb, As, Mg, P, and S ions) remain in the slightly acidic mother liquor. Tungsten, however, is an exception, as most of it is coprecipitated with the polymolybdate. The precipitates also contain an increased amount of chloride ions (0.2 to 0.4%) which are difficult to remove by washing with water.

Recrystallization of the polymolybdate is carried out in order to remove the chloride ions. The salt is dissolved in a 3 to 5% solution of ammonia, at 70 to 80°, in an amount such that a saturated solution is formed (density 1.41 to 1.42). The solution is cooled to 15 to 20° and 50 to 60% of the molybdenum is precipitated as crystalline ammonium paramolybdate $3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O$.

The mother liquor is used for the successive recrystallization of about ten portions of polymolybdate precipitates. Impurities gradually accumulate in the mother liquor and it has to be purified.

The combined precipitation of polymolybdates through neutralization and subsequent recrystallization from an ammoniacal solution yields ammonium paramolybdate of a higher degree of purity than that obtained by evaporation and crystallization of the para-salt. The ammonium paramolybdate prepared by the method contains the following impurities (in% of Mo):

Sn, Pb, Bi, Cd	<0.0001
Zn, Mg, As, P, S, Ni, Cr, Ca	<0.001
Si, Al	<0.003
Fe	<0.005

The isolation of the paramolybdate is carried out in cast-iron reactors coated with acid-resistant enamel and fitted with enamelled anchor-shaped

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stirrers. The reactors are fitted with steam jackets. The addition of acid to the required pH between 2 and 3 is controlled with the aid of a glass electrode pH-meter. The pH is approximately determined by the appearance of a violet color on Congo Red indicator paper.

The acidic mother solution which remains after separation of the crystals still contains 3 to 4% of the initial molybdenum content. This corresponds to a Mo concentration of 6 to 10 g/l. The solution is allowed to stand for a prolonged time, the pH is adjusted to 2, and amorphous polymolybdate precipitates of variable composition are separated and returned to the purification stage. The residual mother liquors contain about 1 g Mo/l. Molybdenum may be isolated from them by sorption on ion-exchange resins (see p. 92).

Extraction of molybdenum from the calcine-leaching residues

Depending on the composition of the concentrate and the method of roasting, the leaching residues contain from 5 to 25% molybdenum. The molybdenum is in the form of calcium and iron molybdates, MoO_2 and non-oxidized molybdenite. In addition, part of the molybdenum is in the form of MoO_4^{2-} ions sorbed on the iron hydroxide and difficult to wash out with water. The remaining components of the residues are: iron oxides and hydroxides, silica, and occasionally tungsten (1 to 5%) as scheelite or wolframite.

The following methods are used for the extraction of molybdenum from the residues: fusion with soda ash, direct leaching with soda ash solutions in autoclaves and digestion with acids.

Fusion with soda ash. The moist residues are mixed with soda ash and the paste-like mixture formed is heated in a furnace for 6 to 8 hours at 700 to 750°. During the fusion all the molybdenum compounds react with the soda ash and are converted into sodium molybdate:

$$CaMoO_4 + Na_2CO_3 \rightarrow Na_2MoO_4 + CaCO_3;$$
$$2FeMoO_4 + 2Na_2CO_3 + {}^1/_2O_2 \rightarrow 2Na_2MoO_4 + Fe_2O_3 + 2CO_2;$$
$$MoO_2 + Na_2CO_3 + {}^1/_2O_2 \rightarrow Na_2MoO_4 + CO_2;$$
$$2MoS_2 + 6Na_2CO_3 + 9O_2 \rightarrow 2Na_2MoO_4 + 4Na_2SO_4 + 6CO_2.$$

The cake is leached with hot water. Iron molybdate is precipitated from the solution which contains sodium molybdate. The iron molybdate is decomposed by aqueous ammonia and the ammonium molybdate solution is recycled.

The iron molybdate is precipitated by the addition of a solution of iron chloride at pH ≈ 3.4 to 5. The precipitates contain a variable amount of Fe_2O_3 and MoO_3, and usually do not correspond to the composition of the molybdate $Fe_2(MoO_4)_3$. The mixture is filtered in a filter press and the moist cake is leached with ammonia water:

$$Fe_2(MoO_4)_3 + 6NH_4OH \rightarrow 3(NH_4)_2MoO_4 + 2Fe(OH)_3.$$

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The processing of molybdenum-containing calcines, including the stage of extraction of molybdenum from the residues by the soda-ash fusion method, is diagrammatically shown in Figure 46. The total extraction of molybdenum into the final product, including the residue processing stage, is 93 to 94%. The discarded residues contain 1 to 1.5% molybdenum.

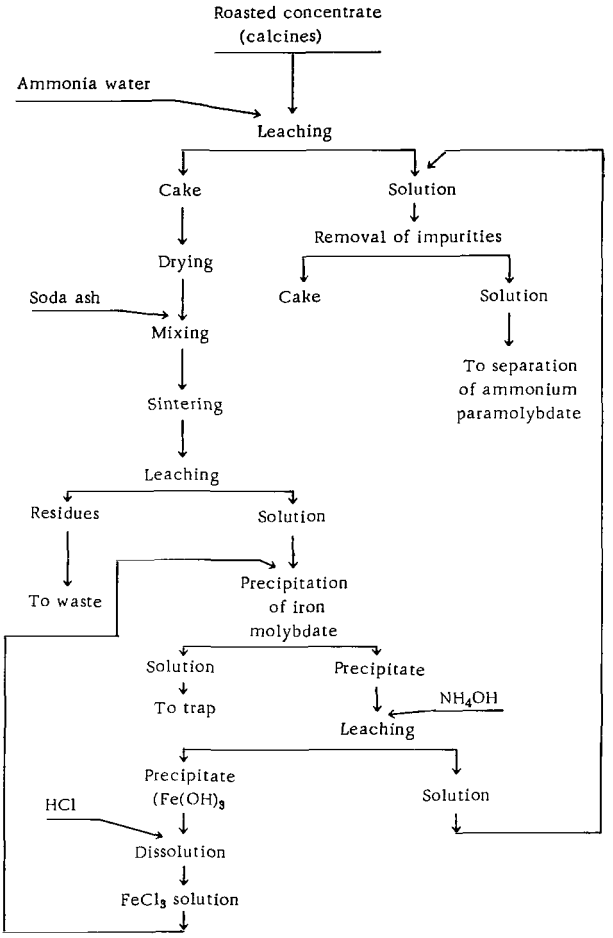

FIGURE 46. Processing of molybdenum calcines including sintering of leaching residues with soda ash.

Leaching with soda ash solutions in autoclaves. Calcines in which molybdenum occurs as $CaMoO_4$ and other molybdates (and which have a very low MoO_2 and MoS_2 content) may be leached directly with soda-ash solutions instead of being fused with soda; the leaching is carried out in autoclaves at 180 to 200° which corresponds to a pressure of about 12 to 15 atm.

Digestion of the cinders with acids /27/ Fusion with soda ash is not a convenient method for processing calcines with an increased tungsten content (3 to 5% W) since all the tungsten passes into solution in the form

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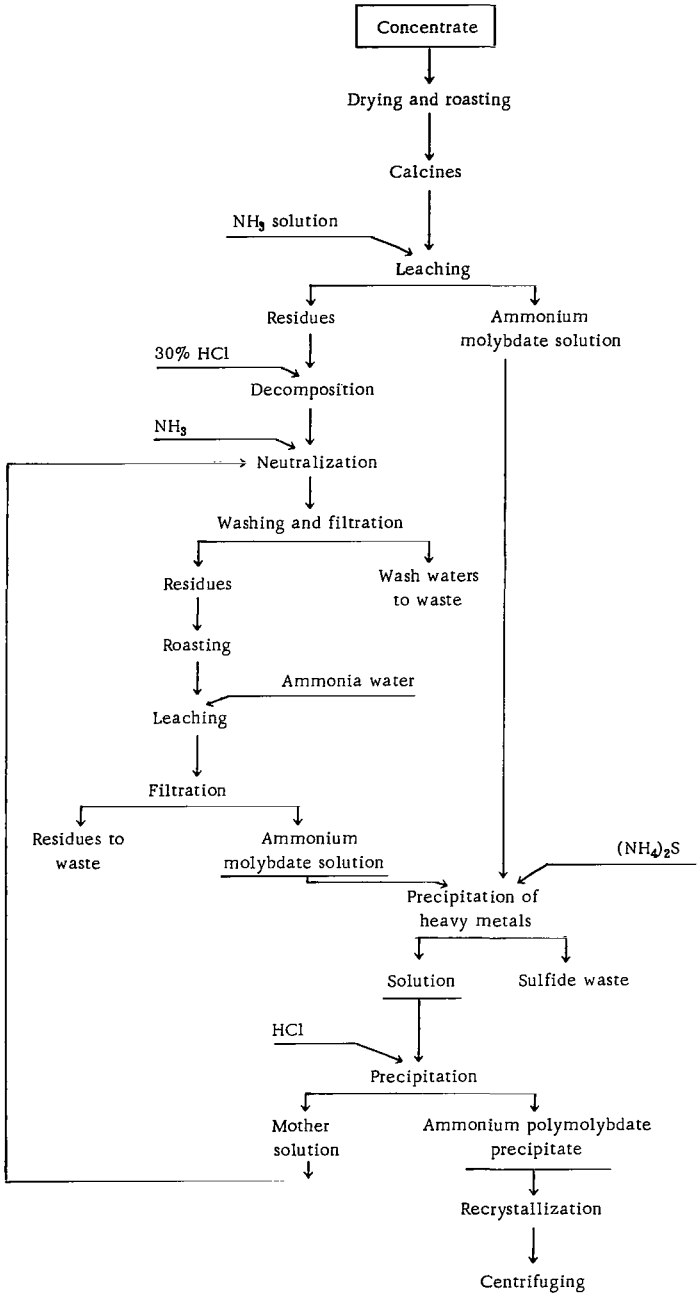

FIGURE 47. Processing of calcines, including acid decomposition of the leaching residues.

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of sodium tungstate. No methods for the separation of tungsten from molybdenum have as yet been developed. In such a case, the calcines are digested with hydrochloric acid (Figure 47). When the calcines are digested with hot 20 to 30% acid, the molybdates are decomposed quantitatively with formation of molybdic acid which readily dissolves in hydrochloric acid. Iron, calcium, copper, and other impurities are also dissolved. The tungsten minerals present in the calcines (scheelite, wolframite) are decomposed only partially by the acid. In addition to these minerals, the residue contains silica, MoO_2 and MoS_2. Neutralization of the acid pulp with ammonia water to pH 2.5 to 3 results in the precipitation of iron molybdate in a mixture with molybdic acid and polymolybdates. Calcium, part of the iron, the copper, and other impurities remain in solution.

The precipitate is separated by filtration. It is then ignited at 580 to 600° in order to oxidize MoO_2 and MoS_2 and is leached with ammonia water. The degree of extraction of molybdenum from the calcines by this method is 80 to 85%.

Extraction of molybdenum into the final product and costing

In the processing of standard molybdenite concentrates, the total extraction of molybdenum into ammonium paramolybdate depends on the impurity content in the initial raw material, the technological process used, and the maintenance of optimum technological conditions. The degree of extraction in manufacturing plants ranges from 93 to 95%. About 1 to 1.5% is lost by roasting, 2 to 2.5% during leaching (including the reprocessing of residues) and 2 to 3% are lost during the purification of solutions and the separation of ammonium paramolybdate.

An analysis of the cost price of ammonium paramolybdate (see below) shows that the main cost item is the raw material (molybdenite concentrate). Hence, it is important to increase the degree of extraction of molybdenum from the concentrate. This requires a reduction of mechanical losses, more efficient trapping of dust, increased extraction of molybdenum from the wash waters and mother liquors and the use of fluidized-bed roasting which yields calcines containing a higher concentration of extractable molybdenum.

The approximate structure of the cost price of one ton of ammonium paramolybdate (in % of the total cost f. o. b. factory) is shown below:

Raw material: molybdenite concentrate	91.8
Chemicals: ammonia water, hydrochloric acid, etc.	2.0
Auxiliary materials: filter cloth, bronze screen, wrapping paper, plywood, etc.	0.2
Power consumption: electrical, fuel, steam, water	1.1
Wages and benefits	1.72
Overheads	3.18
Cost f. o. b. factory	100.0

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19. PROCESSING OF LOW-GRADE CONCENTRATES

The beneficiation of polymetallic molybdenum ores (e. g., copper-molybdenum ores) yields low-grade concentrates and intermediate products which contain, in addition to molybdenum, large amounts of iron, copper, and other impurities. In such materials molybdenum is present both as molybdenite and as the oxidized minerals, powellite and molybdite.

The molybdenum concentration in the low-grade concentrates ranges from ~ 5 to ~ 20% in the presence of large amounts of copper, iron and other impurities. For instance, the low-grade molybdenite concentrates obtained in the concentration of copper-molybdenum ores from a certain deposit had the following approximate composition: 15 to 20% Mo, 3 to 5% Cu, 12 to 15% SiO_2, 10 to 15% Fe, and 20 to 25% S. Low-grade concentrates containing 5 to 6% molybdenum are obtained by concentration of oxidized ores containing powellite.

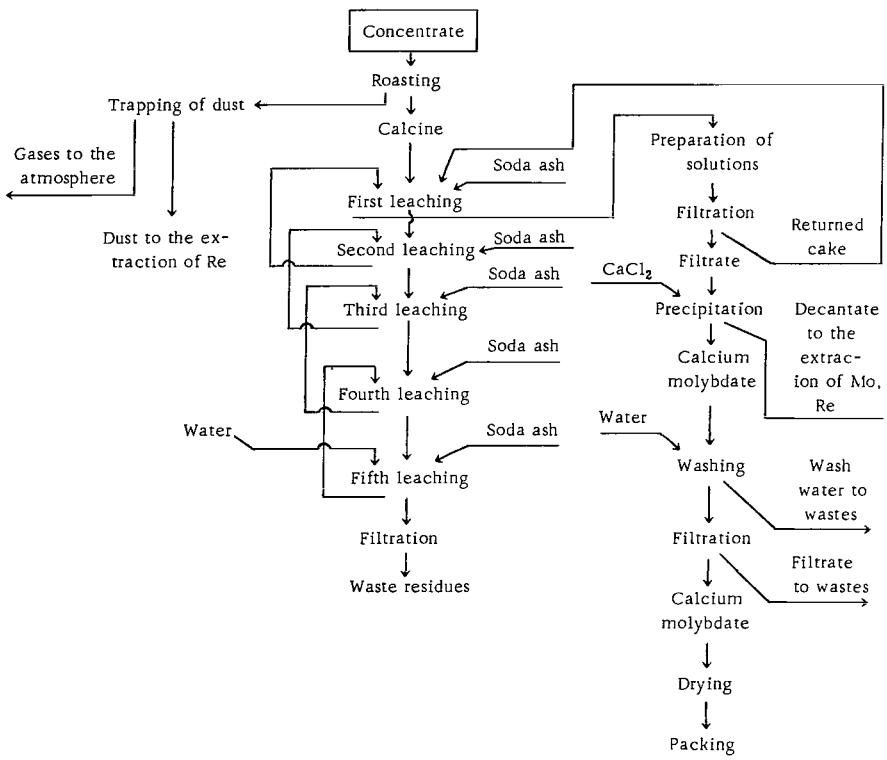

FIGURE 48. Production of calcium molybdate from low-grade molybdenum concentrates.

The processing of intermediate copper-molybdenum products and low-grade powellite concentrates is shown in Figure 48. The processing

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includes roasting of sulfide concentrates, leaching with soda ash solutions and precipitation of technical grade calcium molybdate from solution /15/.

In order to ensure a high degree of extraction of the molybdenum, the calcines from the roasting of low-grade sulfide concentrates and powellite concentrates are leached with soda solutions which differ from ammonia water in that they readily decompose all molybdates.

Leaching. The following reactions take place during leaching with soda solutions:

$$MoO_3 + Na_2CO_3 = Na_2MoO_4 + CO_2;$$
$$2CuMoO_4 + 2Na_2CO_3 + H_2O = 2Na_2MoO_4 + CuCO_3 \cdot Cu(OH)_2 + CO_2;$$
$$FeMoO_4 + Na_2CO_3 + H_2O = Na_2MoO_4 + Fe(OH)_2 + CO_2;$$
$$CaMoO_4 + Na_2CO_3 \rightleftarrows Na_2MoO_4 + CaCO_3.$$

A part of the silica, phosphorus, arsenic, and a fraction of the copper in the concentrates are dissolved together with the molybdenum. Copper is probably dissolved in the form of rather unstable complexes of the type $xCuCO_3 \cdot yNa_2CO_3$. However, if the solution at the end of the leaching is neutral or slightly alkaline, copper carbonate complexes are decomposed and the copper is precipitated as basic carbonates. Most of the silica is also precipiated under the same conditions (hydrolysis of Na_2SiO_3 with precipitation of H_2SiO_3).

An 8 to 10% soda solution is used for leaching, which is carried out in 4 to 5 countercurrent stages (see Figure 48). This results in a better utilization of the soda and permits the removal of solutions which are neutralized to a pH of 8 to 8.7 by fresh portions of the material to be leached. The leaching is carried out in iron reactors fitted with stirrers and heated by dry steam which passes through a steam jacket or coil. The filtered solutions containing 50 to 70 g of molybdenum per liter are sent to precipitation of calcium molybdate.

Precipitation of calcium molybdate. The addition of calcium chloride to the sodium molybdate solution precipitates calcium molybdate. The precipitation is carried out in wood or rubber-lined iron vats at 80 to 90°. The degree of precipitation depends on the pH of the solution, the amount of precipitant added and the initial molybdenum concentration. In order to precipitate at least 97 to 98% of the molybdenum, the process must be carried out in neutral or weakly-alkaline solution, using a small (10 to 15%) excess of calcium chloride which prevents contamination of the precipitate by calcium sulfate. The white, fine crystalline calcium molybdate precipitate is washed with water to remove sulfates and is then separated by filtration and ignited at 600 to 700° in muffle furnaces.

TABLE 17

Chemical composition of standard calcium molybdate

Brand	Minimum molybdenum content, %	Maximum impurity contents, %		
		S	Ca	P
MDK_1	44.0	0.20	22	0.10
MDK_2	44.0	0.23	24	0.20

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The approximate chemical composition of calcium molybdate used in ferrous metallurgy for the introduction of molybdenum into steel and in the smelting of ferromolybdenum is shown in Table 17.

The concentration of molybdenum in the mother liquor from the precipitation of the calcium molybdate is about 1 g/l. Molybdenum is extracted from these solutions by sorption on ion-exchange resins. The sorption is carried out from weakly-acidic solutions (pH 2 to 3), using the anionic resin of AN-1 brand. The sorption capacity of this resin for molybdenum is 20 to 22%. The molybdenum is eluted with a solution of ammonium hydroxide, and the elution yields a solution containing 50 to 70 g of molybdenum per liter.

20. PRODUCTION OF METALLIC MOLYBDENUM

All the methods for the production of metallic tungsten (see previous chapter) can also be applied to the production of molybdenum. Molybdenum trioxide may be reduced to the metal by hydrogen, carbon and carbon-containing gases, as well as by thermal reduction with aluminum and silicon.

The production of pure molybdenum powder (which is then converted to the solid metal) is based on the reduction of MoO_3 with hydrogen.

Pure molybdenum trioxide, which is the starting material for the production of molybdenum powder, is prepared by ignition of ammonium paramolybdate at 450 to 500° in muffle or rotary tube furnace (see Figure 11).

Reduction of molybdenum trioxide with hydrogen

The reduction of molybdenum trioxide with hydrogen is analogous to the reduction of WO_3 described above. There are, however, some differences in the conditions of the reduction.

The reduction is a three-stage process, corresponding to the existence of three molybdenum oxides:

$$4MoO_3 + H_2 \rightleftarrows Mo_4O_{11} + H_2O; \quad (1)$$

$$Mo_4O_{11} + 3H_2 \rightleftarrows 4MoO_2 + 3H_2O; \quad (2)$$

$$MoO_2 + 2H_2 \rightleftarrows Mo + 2H_2O. \quad (3)$$

The equilibrium conditions for these reactions are slightly different from those for tungsten. The equilibrium constant of all these reactions is expressed by the ratio of the equilibrium partial pressures of water vapor and hydrogen:

$$K_p = \frac{p_{H_2O}}{p_{H_2}}.$$

The equilibrium constants for the reduction of MoO_3 at 400 to 700° according to reactions (1) and (2) are higher than those for the reduction of WO_3. This means that for an equal moisture content in the hydrogen, the first reduction stage ($MoO_3 \rightarrow MoO_2$) takes place at temperatures lower than those required for the reduction of WO_3 to WO_2.

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TABLE 18

Equilibrium constants of the reduction of MoO_2 and WO_2 by hydrogen

Temperature, °C	$K_p = \frac{p_{H_2O}}{p_{H_2}}$	
	$MoO_2 \rightarrow Mo$	$WO_2 \rightarrow W$
700	0.38	0.40
760	0.40	0.51
850	0.57	0.72
950	0.72	1.0
1100	1.13	1.44

The equilibrium constant for the reduction of MoO_2 by hydrogen (reaction (3)) is lower than that for the reduction of WO_2; therefore at a given hydrogen : water vapor ratio, the reduction of MoO_2 to the metal occurs at higher temperatures than that of WO_2 (see Table 18).

In accordance with the above, the first stage in the reduction of MoO_3 is carried out at low temperatures (about 450 to 550°) while the third stage is carried out at 1000 to 1100°.

In industrial practice the reduction of molybdenum trioxide is carried out in two or three stages.

In the first stage ($MoO_3 \rightarrow MoO_2$) the temperature along the furnace tube rises from 450 to 650°; the formation of MoO_2 must be virtually completed before the temperature reaches 550° since the intermediate molybdenum oxide and MoO_3 form a eutectic which melts at 550 to 600°.

In the second reduction stage ($MoO_2 \rightarrow Mo$) the temperature along the furnace tube changes from 650 to 950°. The molybdenum powder from the second reduction usually contains 0.7 to 2% oxygen. To eliminate this oxygen a third reduction is carried out at 1000 to 1100°.

The capacity of the boats during the second reduction is about twice and in the third reduction about five times that of the first reduction. This is due to the difference between the bulk density of MoO_3 (0.4 to 0.5 g/cm^3), MoO_2 (1 to 1.5 g/cm^3), and Mo ($\sim$ 2.5 g/cm^3).

The first and second reductions are carried out in furnaces with 9 to 11 chromium-nickel steel tubes. These furnaces have been described in the chapter on tungsten (see Figure 13).

At 1000 to 1100° the resistance of the chromium-nickel steel tubes and the nichrome heaters to the effect of air is noticeably lower than at lower temperatures. The third reduction is therefore carried out in tube furnaces with a hermetically-sealed jacket which is filled with hydrogen in order to protect the tubes and heaters from oxidation.

The molybdenum powder obtained after the third reduction contains about 0.25 to 0.3% oxygen. Its approximate granulometric composition is as follows:

Particle size, μ	> 0.6	0.6 — 1.2	1.2 — 1.8	1.8 — 2.4
Fraction, %	40 — 60	20 — 30	10 — 20	1 — 3

The average particle size of the powder is 0.5 to 2 μ. This is less than the particle size of tungsten powder. This is due to the low temperature of the first reduction stage and the consequent absence of noticeable vaporization of the oxides (see p. 43).

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The first reduction stages have lately been carried out in continuous rotary-drum furnaces, resembling those described in the chapter on tungsten.

21. PRODUCTION OF SOLID, DUCTILE MOLYBDENUM

Solid molybdenum is prepared by powder metallurgy techniques or by the recently developed arc-melting method.

Powder metallurgy method

The nature of the powder metallurgy method has been described in the chapter on tungsten. We shall deal here only with some special features of this process as applied to the production of ductile molybdenum.

In the production of relatively small bars, with a cross section between 2 and 16 cm^2 and a length of 450 to 600 mm, the molybdenum powder is pressed in steel dies at 3 tons/cm^2. The pressed molybdenum bars are stronger than similar tungsten bars, owing to the finer particle size of the molybdenum powders and also to the fact that they possess some plasticity.

The presintering and high-temperature sintering of the bars is carried out in the same equipment as that used in the production of tungsten.

After a presintering in hydrogen at 1100 to 1200°, the bars are sintered at high temperatures, the maximum temperature being 2200 to 2400°.

In the case of bars with a cross section of 18× 18 mm the maximum current applied ($\sim$ 90% of the fusion current) is about 4500 amp. As a result of the fine particle size, the bars contract rapidly. Contraction is complete within 10 to 15 minutes at the maximum temperature. The porosity of the bar is reduced from 40% for the pressed bar to 10 to 15%. The sintered bars have a grain size corresponding to 2500 to 5000 grains/mm^2.

Large bars with a cross section of 40× 40 and 60×60 mm are sintered in installations operating under more drastic conditions, viz., at currents of 8000 to 12,000 amp. The temperature is increased gradually, over 60 to 80 minutes, to the maximum temperature. The sintering time at this temperature is 50 to 70 minutes. The method cannot be used for the production of larger bars since direct heating of larger bars by the passage of a current is accompanied by a large temperature drop from the center to the surface of the bar, resulting in nonuniform properties of the bar across its section. It is difficult, moreover, to obtain a uniform density on pressing large bars in steel dies.

Uniform large bars, weighing 30 to 100 kg, are produced by hydrostatic pressing and such bars are sintered by indirect radiation heating.

In hydrostatic pressing the metal powder is contained in an elastic (e. g., rubber) shell which is placed in a hermetically-sealed compression chamber and water (or some other liquid) under pressure is applied (Figure 49). A pressure of $\sim$ 1500 kg/cm^2 is created in the hydrostatic chamber and the powder is subjected to uniform compression in all directions.

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In contrast to conventional pressing in a steel die, hydrostatic compression is distinguished by the absence of friction between the powder and the die walls. It thus eliminates nonuniformity in the pressed bar.

In order to obtain regular-shaped bars, e. g., a cylindrical or rectangular cross section, the rubber shell filled with the powder is placed in a perforated steel case in the shape of a tube or a rectangular cross section, the rubber shell filled with the powder is placed in a perforated steel case in the shape of a tube or a rectangular box /16/.

Large bars are sintered in muffle furnaces with molybdenum heaters (see Figure 50).

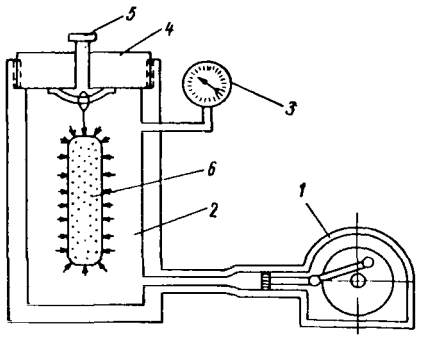

FIGURE 49. Hydrostatic pressing machine.

1 — high-pressure pump; 2 — chamber; 3 — manometer; 4 — closing device (lid); 5 — pressure-release valve; 6 — pressed bar in elastic shell.

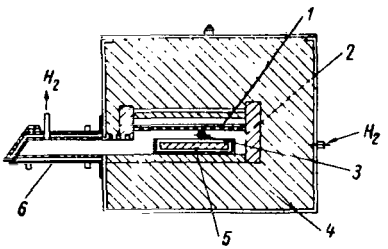

FIGURE 50. Muffle furnace with molybdenum heaters for sintering large molybdenum bars.

1 — molybdenum heaters, 2 — refractory lining; 3 — opening for the measurement of the temperature, 4 — thermal insulation, 5 — molybdenum bar, 6 — water jacket.

Because of the high sintering temperature, the furnace is lined with alumina and zirconia refractories. The sintering temperature may be reduced to 1600 to 1700° by increasing the duration of sintering and conducting it in an atmosphere of moist hydrogen obtained by bubbling hydrogen through water at 20 to 40°. Sintered bars with a density of up to 10 g/cm^3 are obtained by holding for several hours at 1600 to 1700°.

In addition to muffle furnaces, induction furnaces may also be used for sintering large bars.

The melting of molybdenum /8, 17/

Owing to the need for large bars for the drawing of tubes, rolling of large sheets and for other products, an arc-melting method which permits the production of ingots weighing 500 to 2000 kg has been developed.

In all modern arc furnaces the melting is carried out in vacuo, using a consumable molybdenum electrode and cooled copper crucibles (molds). Because of the high thermal conductance of copper and the rapid heat removal, the liquid metal coming into contact with the crucible walls solidifies and thus no interaction takes place between the copper and the molybdenum. The metal is melted in the flame of an arc created between

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the upper electrode (consumable molybdenum electrode) and the lower electrode which consists of the molten metal in the copper mold. A direct current is used for melting, the consumable electrode being used as the cathode and the melt as the anode.

The current is rectified with the aid of generators or large selenium or germanium rectifiers (8000 amperes or more).

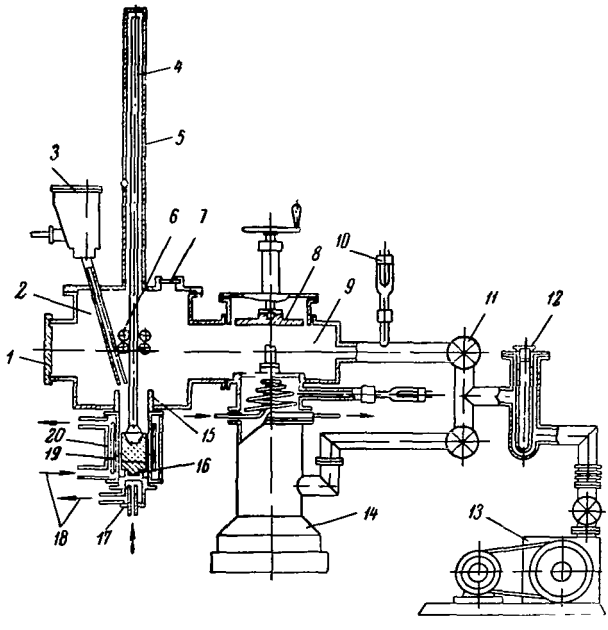

FIGURE 51. Vacuum arc furnace melting of molybdenum.

1—window; 2—melting chamber; 3—hopper for the supply of alloying additives; 4—consumable molybdenum electrode; 5—tube; 6—roller feed mechanism; 7—peephole; 8—valve; 9—vacuum block; 10—vacuum-measuring lamp (LT-2); 11—vacuum valves; 12—liquid nitrogen trap; 13—rotary (preliminary) vacuum pump; 14—diffusion pump; 15—ceramic ring; 16—bottom plate; 17—cooled bottom of crystallizer; 18—cooling-water connections; 19—solenoid; 20—cooled copper crystallizer.

In the most extensively used arc furnaces the electrode is prepared in advance from sintered molybdenum bars. The bars are connected by butt welding to electrodes 1 to 2.5 m long. The electrodes are then joined into packs, 4 to 16 bars or even more being joined together depending on the size of the crystallizers. The consumable electrode is moved during melting with the aid of a rod (which also serves as the current carrier) at whose end the electrode is fastened. It may also be moved by a roller drive mechanism (Figure 51) /17/.

A molybdenum disc is placed on the bottom of the crystallizer before the melting. The furnace is evacuated to a pressure of 10^{-3} to 10^{-4} mm Hg and the electrode is lowered to strike the arc. In some furnaces the bottom

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plate of the crystallizer descends together with the ingot as the melting proceeds (Figure 52) /8/.

A constant arc voltage of 30 to 40 V is maintained by means of automatic control of the distance between the electrodes (i. e., arc length), which ranges from 10 to 25 mm depending on the melting conditions.

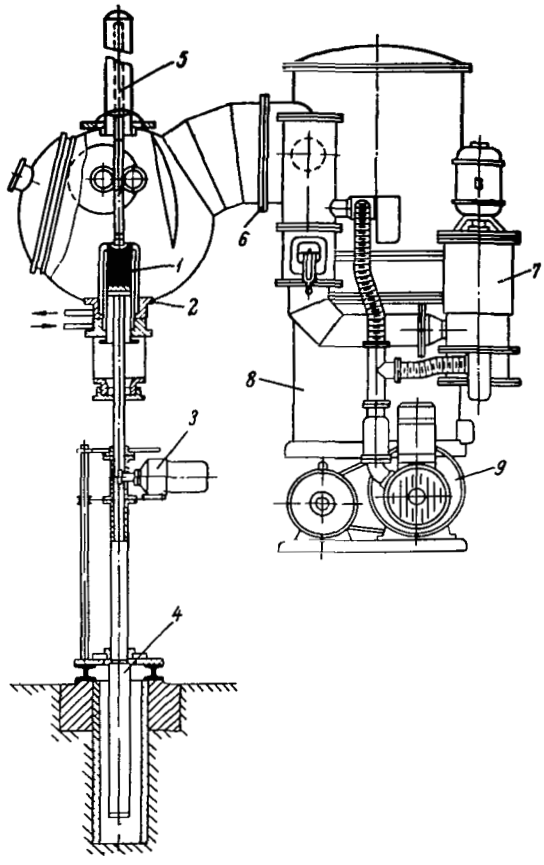

FIGURE 52. Furnace with moving ingot for melting molybdenum.

1—ingot electrode; 2—water-cooled copper mold; 3—ingot depression device; 4—device for extracting the ingot from the mold; 5—consumable electrode; 6—connection to the vacuum line; 7—booster pump; 8—diffusion pump; 9—rotary pump.

A magnetic coil (solenoid) which is placed off-center with respect to the crystallizer is used to control the shape of the arc and to prevent the formation of side arcs (e. g., between the electrode and the crucible walls). The magnetic field of the solenoid also causes mixing of the metal.

In order to obtain ductile metal, the molybdenum must be deoxidized during melting. The oxygen content of the molten molybdenum must not

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exceed 0.002%. Carbon, which is added to the consumable electrode during its manufacture serves as the deoxidizer. Zirconium and titanium are also used as deoxidizers. The residual carbon which constitutes a few hundredths of one percent of the metal is in the form of isolated carbide occlusions and does not interfere with hot forging of molybdenum ingots.

The alloying additives may be introduced as components of the consumable electrode or may be fed into the arc space (as shown in Figure 51). Since only a small fraction of the metal is in the molten state during arc melting, the distribution of alloying additives is nonuniform. A second melting is usually carried out in order to obtain ingots of uniform composition.

The melting rate depends on the cross section of the consumable electrode and on the melting conditions (current strength, the number of ampere-turns in the solenoid, the arc voltage). Under optimum conditions (a current of 4300 amp, a solenoid with 2500 to 3000 ampere-turns, and a voltage of 38 to 39 V) the melting rate of an electrode with a cross section of 30.7 cm^2 is 75 mm/minute. The consumption of electrical energy in melting is about 1 kilowatt-hour per kg metal.

The ingots formed have a coarse crystalline structure (their grain size is 0.05 to 0.1 mm) which interferes with pressure molding. However, processes have been developed to produce sheets, wires, tubes, and other molybdenum products from these ingots.

In addition to arc melting, electron-beam melting has been recently used for melting refractory metals including molybdenum. The nature of the electron-beam melting process will be discussed in the chapter on tantalum and niobium.

Electron-beam melting increases the purity of the molybdenum from 99.8 to 99.99%. A decrease in the concentration of many impurities occurs: O, N, C, Si, P, As, Fe, Cu, Ni, Mn, Co, and Ti.

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Chapter III

TANTALUM AND NIOBIUM

22. GENERAL DATA ON TANTALUM AND NIOBIUM

In 1801 an English chemist, Hatchett, discovered the element niobium (columbium) in a mineral from Columbia. He called it "columbite". Tantalum was discovered in two minerals, one from Sweden and the other from Finland, by a Swedish chemist, Ekeberg, in 1802. The name tantalum was chosen because of the "tantalizing difficulties" encountered when attempting to dissolve the oxide of the new element in acids.

Later, the two new elements were considered identical. In 1844 Rose, a German chemist, proved that the mineral columbite contained two different elements: niobium, deriving its name from Niobe, symbol of maternal sorrow and the daughter of Tantalus, and tantalum. In 1865 Marignac showed that tantalum and niobium could be separated utilizing the difference in the solubilities of the fluoride complexes of these salts, a method which found industrial application and is in use even today.

For a long time all attempts to produce pure compact metallic tantalum and niobium met with failure. Pure tantalum was produced for the first time in 1903 and niobium in 1907 by von Bolton. The commercial production of tantalum dates from 1922, that of niobium from 1928.

Properties of tantalum and niobium

Tantalum and niobium belong to Group V of the periodic table. The chemical and physical properties of these two elements are similar. They almost always occur together in ores. Consequently, their metallurgy is usually discussed jointly.

Tantalum and niobium are steel-gray metals; tantalum has a faint blue hue. The pure metals are ductile and may be rolled into thin foils of 0.01 mm thickness without heating or intermediate annealing.

Some of the physical properties of tantalum and niobium are listed in Table 19. It should be noted that their melting points are higher and their electron work functions lower than those of other refractory metals (tungsten and molybdenum). The latter property characterizes the electron emission capacity of the metals. It is of importance for the use of tantalum and niobium in vacuum tube industries. Both metals, especially niobium, have a high superconductance transition temperature.

Tantalum and niobium are not affected by air at room temperature. Oxidation begins with the formation of an iridescent film when the metals

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are heated to 200 to 300°. Rapid oxidation with the formation of Nb_2O_5 and Ta_2O_5 takes place above 500°.

TABLE 19

Physical properties of tantalum and niobium

Properties	Tantalum	Niobium
Atomic number	73	41
Atomic weight	180.88	92.91
Density, g/cm^3	16.65	8.57
Lattice type	b. c. c. a = 3.296 Å	b. c. c. a = 3.294 Å
Temperature, °C		
melting point	3000 ± 50	2470 ±10
boiling point	~5300	~4930
Specific heat, cal/g °C at:		
0—100	0.034	0.065
1600	0.041	0.083
Thermal conductivity (at 20—100°), cal/cm·sec, °C	0.13	0.13
Linear expansion coefficient (0 to 100°C)	$6.5 \cdot 10^{-6}$	$7.1 \cdot 10^{-6}$
Electrical resistivity (20° C) ohm·cm	$12.5 \cdot 10^{-6}$	$13.2 \cdot 10^{-6}$
Superconductance transition temperature, °K	4.38	9.17
Temperature coefficient of electrical resistivity (0 to 100° C)	0.00382	0.00395
Electron work function, eV	4.12	4.01
Total radiation (watt/cm^2) at:		
1330° C	7.2	6.3
1730° C	21.2	19
1930° C	33	30
2330° C	75	70
2530° C	108	—
Thermal neutron cross section, barns	21	1.15
Tensile strength of annealed sheet, kg/mm^2	35—50	30—35
Elongation of annealed sheet, %	25—45	Up to 49
Modulus of elasticity, kg/mm^2	19000	10600
Microhardness of annealed sheet (30 g load), kg/mm^2	108	88

Tantalum and niobium are characterized by their ability to absorb gases such as hydrogen, nitrogen, and oxygen. The presence of small amounts of these elements strongly affects the mechanical and electrical properties of the metals. The absorption of hydrogen at low temperatures is slow; it occurs at the maximum rate at about 500° in tantalum and 360° in niobium. At these temperatures both absorption and the formation of chemical compounds such as NbH and TaH take place. Absorbed hydrogen makes the metal brittle. It may be expelled almost quantitatively by heating in vacuum above 600°, the original mechanical properties thus being restored.

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Tantalum and niobium absorb nitrogen at temperatures as low as 600°. At higher temperatures the nitrides NbN and TaN, with melting points of 2300 and 3087° respectively, are formed.

Carbon and carbon-containing gases interact with the metals at high temperatures (1200 to 1400°) with the formation of the hard, refractory carbides, TaC, melting at 3880°, and NbC, melting at 3500°

Tantalum and niobium combine with boron and silicon yielding the hard, refractory borides and silicides, NbB_2 (mp 2900°), TaB_2 (mp 3000°) and $TaSi_2$ (mp 2400°).

Tantalum and niobium are not attacked by hydrochloric, sulfuric, nitric, phosphoric or organic acids at any concentration at temperatures below 100 to 150°. The resistance of tantalum to hot hydrochloric and sulfuric acids is higher than that of niobium. The metals are soluble in hydrofluoric acid, and dissolve very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum and niobium are less resistant to alkalies. Hot solutions of alkali hydroxides cause noticeable etching of the metals, which are oxidzed rapidly by fused alkali hydroxides and soda ash with the formation of sodium tantalates and niobates.

The properties of tantalum and niobium compounds

The chemical compounds of pentavalent niobium and tantalum are the most stable and useful. Compounds in which the metals are in the di-, tri- and tetravalent state are also known.

Oxides. The higher oxides Nb_2O_5 and Ta_2O_5 are usually obtained as intermediate products in the commercial processing of ores. Both oxides are white; Nb_2O_5 becomes yellow upon heating, but the yellow color disappears upon cooling. Some properties of the oxides are shown below:

	Nb_2O_5	Ta_2O_5
Density	4.55	8.71
Melting point, °C	~1510	~1620
Heat of formation, kcal/mole	455.2	488.8

The large difference between the densities of the oxides permits an approximate evaluation of the chemical composition of a mixture of the oxides from density measurements.

The oxides Nb_2O_5 and Ta_2O_5 have distinctly acid properties. When fused with alkalies they yield niobates and tantalates, i. e., salts of niobic and tantalic acids. Precipitates consisting of the hydrated oxides $Ta_2O_5 \cdot xH_2O$ and $Nb_2O_5 \cdot xH_2O$ are formed when acid solutions containing tantalum and niobium are neutralized or when the niobates and tantalates of alkali metals are treated with acids. The hydrated oxides dissolve in concentrated hydrochloric and sulfuric acids, but are precipitated due to hydrolysis when the solutions are diluted.

Two lower oxides of niobium are known: NbO_2 (black) and NbO (gray powder); they are formed when Nb_2O_5 is reduced by hydrogen or carbon. The lower tantalum oxides TaO_2 and Ta_2O have been mentioned in the literature, but their existence has not been confirmed in more recent studies.

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Niobates and tantalates. Niobic and tantalic acids have not been isolated in the free state, but salts of the meta and ortho acids, HRO_3 and H_3RO_4, where R is Nb or Ta, are known to exist.

In addition to the ortho- and metaniobates (-tantalates), there also exist polyniobates and polytantalates whose composition corresponds to the general formula $xMe_2O \cdot yR_2O_5$ where Me_2O is an alkali metal oxide and R is Ta or Nb. Depending on the amount of the alkali hydroxide used, the fusion of niobium or tantalum pentoxide with alkali hydroxides yields either the ortho salts Me_3RO_4 or the meta salts $MeRO_3$. The meta salts are also formed in the interaction of tantalum or niobium pentoxide with solutions of sodium or potassium hydroxide at 150 to 200° /20, 21/. The anhydrous meta salts are virtually insoluble in water. The ortho salts dissolve in water with hydrolytic decomposition which results in the formation of complex hydrated polyniobates (tantalates) of various composition /21/:

$$4Me_2O \cdot 3R_2O_5 \cdot nH_2O \text{ (or } Me_8R_6O_{19} \cdot nH_2O);$$
$$7Me_2O \cdot 5R_2O_5 \cdot nH_2O \text{ (or } Me_7R_5O_{16} \cdot nH_2O);$$
$$7Me_2O \cdot 6R_2O_5 \cdot nH_2O \text{ (or } Me_{14}R_{12}O_{37} \cdot nH_2O).$$

Thus, for instance, the following polyniobates (polytantalates) are formed when Nb_2O_5 or Ta_2O_5 is fused with an alkali hydroxide and the cake is then treated with water:

$$4K_2O \cdot 3Nb_2O_5 \cdot 16H_2O;\ 4K_2O \cdot 3Ta_2O_5 \cdot 16H_2O;$$
$$7Na_2O \cdot 6Nb_2O_5 \cdot 32H_2O;\ 4Na_2O \cdot 3Ta_2O_5 \cdot 25H_2O.$$

The potassium salts dissolve readily in water, while the sodium salts are sparingly soluble. According to Spitsyn and Lapitskii, the solubility of sodium niobate (the 7 : 6 salt) in water is 15 g/l at 20° and 26 g/l at 90°. The presence of an alkali in the solution causes a sharp drop in the solubility. The solubility of the tantalum salt in water at 14° is about 0.2 g/100 ml /8/.

Tantalum and niobium fluorides. The higher niobium and tantalum oxides dissolve in hydrofluoric acid with the formation of solutions of the fluorides NbF_5 and TaF_5; in the presence of an excess of hydrofluoric acid these fluorides yield complex acids:

$$TaF_5 + 2HF \rightleftarrows H_2[TaF_7],$$
$$NbF_5 + 2HF \rightleftarrows H_2[NbF_7].$$

In a dilute acid solution (at HF concentrations below 7%) NbF_5 hydrolyzes with formation of an oxyfluoride $NbOF_3$ and the corresponding oxyfluoroniobic acid $H_2[NbOF_5]$. The addition of potassium fluoride to a solution containing tantalum or niobium fluoride results in the formation of complex fluorine-containing salts (K_2TaF_7, K_2NbF_7, K_2NbOF_5) which play an important role in the manufacture of tantalum and niobium. Potassium oxyfluoroniobate crystallizes from solutions with an HF concentration below 7% as platelets of the monohydrate ($K_2NbOF_5 \cdot H_2O$). The compounds K_2TaF_7 and K_2NbF_6 crystallize from solutions as isomorphous needle-shaped crystals. The solubility of K_2TaF_7 is much lower than that of $K_2NbOF_5 \cdot H_2O$. This fact is utilized in the separation of niobium from tantalum.

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The anhydrous tantalum and niobium fluorides NbF_5 and TaF_5 are very hygroscopic, deliquescent substances which fume in air. They are formed when metallic tantalum or niobium or their pentoxides are treated with fluorine or hydrogen fluoride; the fluorides have low melting points.

	NbF_5	TaF_5
Melting point, °C	80	95
Boiling point, °C	234.9	229.2

Niobium and tantalum chlorides. The chlorides $NbCl_5$ and $TaCl_5$ are formed when the metals or the oxides are treated with chlorine or other chlorinating agents. Niobium oxychloride $NbOCl_3$ is preferentially formed when Nb_2O_5 is treated with chlorine in the presence of carbon.

The chlorides have low melting and boiling points:

	$NbCl_5$	$TaCl_5$
Melting point, °C	204.7	216.5
Boiling point, °C	248.3	234.0
Density	2.75	3.68

Niobium oxychloride volatilizes at about 400°. The vapor pressure of $NbOCl_3$ at 330° is 482 mm Hg.

The chlorides are very hygroscopic and tend to hydrolyze. Precipitates of white hydrated oxides are formed in aqueous solutions as a result of hydrolysis:

$$2TaCl_5 + (x + 5)H_2O = Ta_2O_5 \cdot xH_2O + 10HCl.$$

Lower niobium and tantalum chlorides are also known: $NbCl_4$, $NbCl_3$, $TaCl_4$, $TaCl_3$, and $TaCl_2$. They can be prepared by the reduction of the higher chlorides with hydrogen or metals such as aluminum. $NbCl_5$ is reduced more readily than $TaCl_5$; this is the principle of some methods for the separation of niobium and tantalum.

Peracids of niobium and tantalum. The freshly-precipitated hydrated oxides of niobium and tantalum dissolve in a mixture of dilute sulfuric acid and hydrogen peroxide yielding peracids whose composition is either HRO_4 or H_3RO_8, depending on the number of peroxide groups.

There exist salts of peracids with a larger number of peroxide groups, niobate and tantalate peroxides of the type K_3NbO_8 and K_3TaO_8. Solutions of the peroxide compounds are colorless.

Complexes with organic acids. Soluble complex acids and their salts are formed by the reaction of niobic or tantalic acid with oxalic, tartaric, and other similar acids. In these complexes, part of the oxygen in the niobic or tantalic acid is replaced by the organic acid radical. For instance, the complex is formed with oxalic acid:

$$H_3[RO(C_2O_4)_3], \text{ where } R\text{—Nb or Ta}$$

Niobic and tantalic acids react with tannin (an ester of glucose and digallic acid) to form an adsorption complex resulting from the neutralization of oppositely charged colloidal particles. Tannin has a positive charge while the niobium and tantalum compounds are negatively charged. The

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lemon-yellow tantalum complex is precipitated after boiling in a weakly acid solution at pH 3 to 4. The orange-colored niobium complex is precipitated from neutral or very weakly acid solutions in the presence of an excess of tannin. The difference in the conditions of precipitation of the tantalum and niobium complexes permits the separation of tantalum from niobium, a fact which finds use in quantitative chemical analysis.

The complexes of fluoroniobic or fluorotantalic acid with some organic solvents, e.g., tributyl phosphate and methyl isobutyl ketone, are of technological importance (for their composition see p. 125).

Uses of tantalum and niobium

Vacuum-tube technology and electrical technology. Tantalum was used for the first time in 1900 to 1903 for the production of incandescent filaments in electric bulbs, but was subsequently replaced by tungsten in 1909—1910.

The extensive use of tantalum is associated with the development of vacuum-tube technology, including the production of radio, radar and X-ray equipment.

Tantalum and niobium are characterized by a combination of very valuable properties (high melting point, high emissivity, and the ability to absorb gases) which permit their use in the production of vacuum-tube parts. Their ability to absorb gases is utilized in order to maintain high vacuum in radio and other vacuum tubes.

Tantalum and niobium sheets and bars are used for the production of heated parts — anodes, grids, indirectly heated cathodes, and other parts of vacuum tubes and especially of high-power generator tubes. Tantalum-niobium alloys are used for similar purposes.

Recently, tantalum and niobium have found important use in the manufacture of electrolytic condensers and rectifiers. Advantage is taken of the capacity of tantalum and niobium to form stable oxide films during anodic oxidation. The anodic films are stable in acid electrolytes and permit the flow of current in one direction only, from the electrolyte to the metal. The resistivity of Ta_2O_5 films in the non-conducting direction is very high ($7.5 \cdot 10^{12}$ ohm · cm) and its dielectric constant is 11.6.

Solid-electrolyte condensers made of tantalum and niobium are characterized by a high capacitance and small size, by a high insulation resistance, 2 to 3 times higher than that of aluminum condensers, and by the stability of the oxide film. They can be used over a wide temperature range from -80 to +200°. Miniature tantalum condensers are extensively used in radio transmitters, radar setups, and other types of equipment.

The tantalum or niobium components of the condensers are prepared from thin foils or porous plates which are produced by pressing the metallic powder.

Construction of chemical apparatus. The corrosion resistance of niobium and especially of tantalum in acids and other media, together with their high electrical conductivity and ductility, make these metals valuable structural materials for chemical and metallurgical equipment.

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Tantalum and niobium are used for the production of condensers, heaters, lining of vessels, stirrers, and other parts. Tantalum serves instead of platinum in the production of spinnerets for the drawing of synthetic silk threads.

Atomic energy. Niobium is characterized by a combination of properties that satisfy the requirements of atomic energy with respect to structural materials: high melting point, good workability, corrosion resistance, and a relatively low thermal neutron capture cross section of about 1.15 barn.

Below 900° there is almost no interaction between niobium and uranium, so that niobium is used to make the protective shells of uranium fuel elements for nuclear reactors. This permits the use of liquid-metal coolants — sodium or sodium-potassium alloys with which niobium does not react below 600°. In order to increase the service life of uranium fuel elements, the uranium is alloyed with about 7% niobium. The addition of niobium stabilizes the protective oxide film on the uranium and thus increases its resistance to water vapor.

The production of refractory and hard alloys. Niobium and tantalum are components of various refractory alloys used in the turbines of jet engines. The properties of molybdenum, titanium, zirconium, aluminum, copper and their alloys are markedly improved by the addition of niobium or tantalum. Niobium-based refractory alloys have been proposed as a structural material for various parts of jet engines and rockets, specifically for the production of turbine blades, the leading edges of wings, the foreparts of planes and rockets, and the lining of rockets. Niobium and niobium-based alloys may be used at service temperatures of 1000 to 1200°.

Niobium and tantalum carbides are components of some types of tungsten carbide hard cermets for metal cutting.

The production of steels. Tantalum and especially niobium are extensively used as alloying additives in steels. Niobium became of interest in 1933 to 1934 in connection with the discovery of its effect on chromium-nickel stainless steels. The addition of niobium in an amount 6 to 10 times higher than that of carbon in the steel eliminates intercrystalline corrosion of stainless steel and prevents damage to welded joints.

In addition, niobium and tantalum are added to various refractory steels (especially those used for gas turbines) as well as to tool and magnetic steels.

Niobium is added to steels as an alloy with iron (ferroniobium) containing up to 60% Nb. Ferrotantaloniobium with various tantalum : niobium ratios in the alloy is also used.

Other uses. Tantalum wire and sheets are used in bone and plastic surgery, notably in the setting of bones, "patching" skull damage, application of sutures, etc. The metal has no irritating effect on live tissues and does not impede the vital activity of the organism.

Some tantalum and niobium compounds such as fluoride complexes and oxides are used as catalysts in organic synthesis.

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23. MINERALS, ORES, AND ORE CONCENTRATES

The content of niobium in the Earth's crust is $1 \cdot 10^{-3}$% by weight, while that of tantalum is $2 \cdot 10^{-4}$% by weight. Niobium and tantalum almost always occur together in nature. They are components of about 100 different minerals, a large fraction of which consists of very complex salts of niobic and tantalic acids. The minerals contain, in different ratios, iron, manganese, alkali, and alkaline-earth metals as well as many rare elements: lanthanides, titanium, zirconium, throium, uranium, tin, antimony, bismuth, tungsten, and others.

The most important tantalum and niobium minerals may be divided into two groups:

1. Tantaloniobates, which are salts of niobic and tantalic acids. The main minerals in this group are tantalite and columbite.

2. Titano(tantalo)-niobates, which are complex salts of titanic and niobic (tantalic) acids. Almost all minerals in this group contain lanthanides. As in the tantaloniobates, the niobium : tantalum ratio varies within wide limits, but in most cases niobium is predominant. Titanium is the predominant component of some minerals. Among the most important minerals belonging to this group are pyrochlore, loparite, koppite, betafite, and some others.

The compositions and properties of the most important tantalum and niobium minerals are described below.

Tantalite and columbite. Their composition can be expressed by the general formula $(Fe, Mn)[(Ta, Nb)O_3]_2$. Accordingly, the minerals consist of an isomorphous mixture of four salts:

$$Fe(TaO_3)_2,\ Mn(TaO_3)_2,\ Fe(NbO_3)_2 \text{ and } Mn(NbO_3)_2.$$

Minerals with strongly varying ratios of niobium to tantalum and iron to manganese are encountered. The mineral is known as columbite when the predominant component is niobium and tantalite when it is tantalum. The total niobium and tantalum content of the mineral (as $Nb_2O_5 + Ta_2O_5$) is 82 to 86%.

Tantalite and columbite almost always contain titanium, tin, tungsten, and other impurity elements. The minerals are brown-black. Their density is strongly affected by the niobium and tantalum contents. Tantalum-free columbite has a density of 5. The density of tantalite is 8.2. The density increases regularly between these limits with increasing tantalum content of the mineral, and the tantalum and niobium contents of the mineral can be approximately evaluated from the density.

The less abundant minerals belonging to this group are: fergusonite-tantaloniobate of yttrium, erbium and the elements of the cerium group; samarskite-tantaloniobate of iron, calcium, yttrium, and cerium; stibiotantalite — tantaloniobate of antimony, and others.

Pyrochlore is a mineral with a very complex chemical composition. It is a salt of niobic and titanic acids (titanoniobate), containing sodium, calcium, lanthanides, and a number of other rare elements, as cations. In addition, the mineral contains fluorine. Its general formula is $(Na, Ca...)_2(Nb, Ti)_2O_6[F, OH]$. The color of pyrochlore is dark-brown, red-brown, or yellowish-green. Its density is 4.03 to 4.36.

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Microlite is a mineral whose composition is analogous to that of pyrochlore, but with tantalum in place of niobium.

Niobium and tantalum usually occur together in these minerals since pyrochlore and microlite form a series of isomorphous mixtures. The composition of minerals in the pyrochlore-microlite series is very complex and variable:

63—0% Nb_2O_5,	1—6% Na_2O,	2—13.3% $(Ln)_2O_3$
0—70% Ta_2O_5,	0—1.4% K_2O,	0—5.1% Y_2O_3,
2—13.5% TiO_2,	4—18.1% CaO,	0—4.0% SnO_2,
0—5% ThO_2,	0—7.7% MnO	0—5.7% ZrO_2,
0—11.4% UO_2,	0—10% FeO	0—0.3% WO_3,
0—15.5% UO_3	0—9.7% Fe_2O_3	0—6.0% H_2O

The mineral koppite (a calcium, sodium, and cerium niobate) and a series of other minerals also belong to the pyrochlore-type group.

Loparite is a titanoniobate of sodium, calcium, and the lanthanides. Its general formula is $(Na, Ca, Ce...)_2(Ti, Nb)_2O_6$. The variations in its composition are relatively small. The mineral contains 39.2 to 40% TiO_2, 32 to 34 % Ln_2O_3, 8 to 10% $(Nb, Ta)_2O_5$, 4.2 to 5.2% CaO, 7.8 to 9% Na_2O, 2.0 to 3.4% SrO, 0.2 to 0.7% K_2O, and 0.2 to 0.7% ThO_2.

The tantalum content is lower (by a factor of 15) than that of niobium. The mineral is black or gray-black and its density is between 4.75 and 4.89.

The tantalum and niobium deposits are associated mainly with the so-called pegmatites. Pegmatite veins are characterized by a great variety of embedded minerals and by their coarsely-crystalline structure. There are two types of pegmatites : the granite pegmatites and the alkaline nepheline syenite pegmatites. The minerals tantalite and columbite preferentially accumulate in the first type, while minerals of the titano-niobium group (pyrochlore, loparite, etc.) are concentrated in the second type of pegmatites. Tantalite and columbite are concentrated not only in veined deposits but also in some placers. Up to 80% of all the tantalum-niobium concentrates produced outside the USSR originate from placers.

The pyrochlore ores from carbonatite deposits have recently become (1955 to 1956) an important source of niobium. The main non-metalliferous minerals in these ores are calcite, dolomite, ankerite, some silicates (phlogopite, forsterite) apatite and magnetite. In addition to pure niobium pyrochlores, the carbonatite also contains tantalum-containing pyrochlores (hatchettolite) as well as lanthanide minerals — fluoro-carbonates (bastnäsite, parisite) /23/.

The niobium and tantalum contents of ores are usually quite low, the total content of the pentoxides being between 0.003 to 0.1% . In view of the complex nature of most of the deposits, the niobium and tantalum minerals are obtained as by-products in the extraction of other valuable minerals, such as cassiterite, wolframite, lithium minerals, beryl, zircon, etc.

The main method for the beneficiation of ores containing columbite and tantalite is gravitational enrichment (wet jigging, tabling). The usual product is an overall concentrate containing tantalite and columbite, as well as cassiterite, wolframite and some other minerals. Further enrichment is produced by flotation and electromagnetic separation /22/.

The approximate composition of the concentrates is shown in Table 20.

In accordance with the official standards in force in the USSR, first-grade tantalum concentrates must contain at least 60 to 65% Ta_2O_5 and

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not more than 10% Nb_2O_5, while second-grade concentrates must contain at least 40% Ta_2O_5; first-grade columbite concentrates must contain at least 60% Nb_2O_5 and second-grade concentrates at least 50% Nb_2O_5 /22, 23/.

TABLE 20

Approximate composition of tantalite and columbite concentrates, %

Composition	Tantalite	Columbite
Nb_2O_5	12 — 30	50 — 58
Ta_2O_5	53 — 59.6	12 — 18
Fe_2O_3	2.09 — 15.7	10.5 — 19.0
MnO	2.95 — 17.2	2.44 — 8.3
TiO_2	0.25 — 6.4	6.8 — 11.6
SnO_2	0.13 — 0.9	0.1 — 2.7

Gravitational methods (jigging, tabling) are also the main means of enriching pyrochlore and loparite ores. The resulting "crude" concentrates are further enriched to the required concentration by flotation, electromagnetic and electrostatic methods /22/.

According to Soviet standards, the pyrochlore concentrates, which are used mainly for the smelting of ferroniobium, must contain at least 37% $(Nb, Ta)_2O_5$, while loparite concentrates must contain at least 8% $(Nb, Ta)_2O_5$ /22, 23/.

The main western raw material producing countries are: Brazil, Nigeria, Congo (Leopoldville), Mozambique, Australia, USA, Malaya, Norway and Western Germany.

24. PROCESSING OF TANTALUM-NIOBIUM ORE CONCENTRATES

The ore concentrates are usually processed to yield three types of chemical compounds: oxides (Ta_2O_5, Nb_2O_5), fluoride complexes (K_2TaF_7 and K_2NbF_7), and chlorides.

The selection of the technological process for the processing of concentrates is determined by the mineralogical and chemical composition of the concentrate, by the final product required, and by the degree of its purity.

Tantalite and columbite are stable minerals which are virtually not attacked at all by inorganic acids, except hydrofluoric acid. Thus, tantalite (or columbite) concentrates are decomposed by fusion with alkalies (NaOH, KOH) or by digestion with hydrofluoric acid.

The minerals belonging to the titanium-tantalum-niobium group (loparite, pyrochlore) are less stable than tantalite and columbite, but their composition is more complex. Their processing must provide for the separate extraction of all valuable components — niobium, tantalum,

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titanium, and lanthanides. The concentrates of these minerals are decomposed by digestion with acids (H_2SO_4, HF) or by chlorination.

25. PROCESSING OF TANTALITE-COLUMBITE BY FUSION WITH SODIUM HYDROXIDE* /2/

Fusion with sodium hydroxide is a widely used method of decomposition of tantalite (columbite) concentrates. A flow sheet of the production of a mixture of tantalum and niobium oxides by this method is shown in Figure 53.

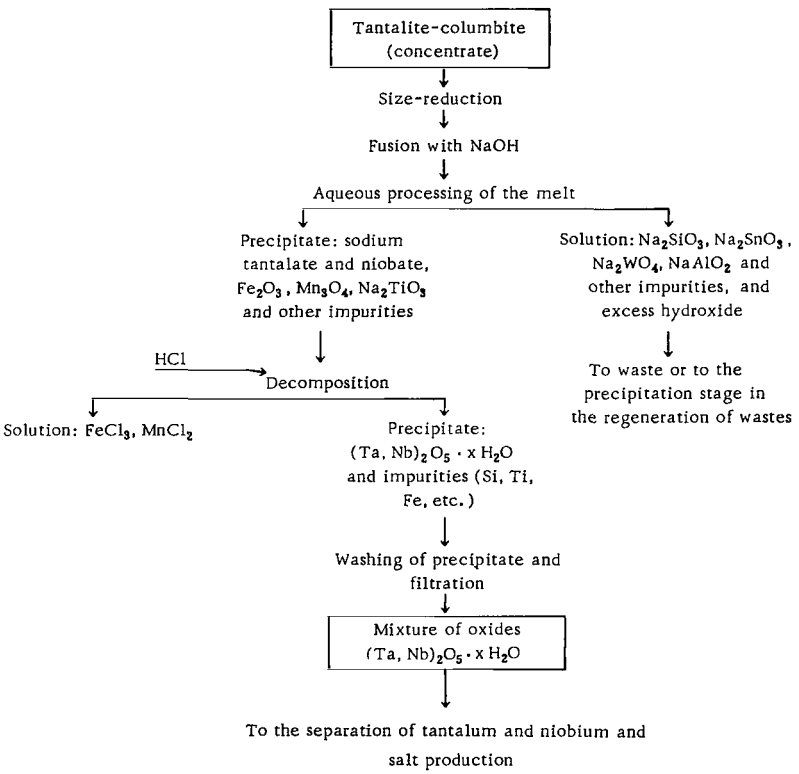

FIGURE 53. Production of a mixture of tantalum and niobium oxides by fusion of the concentrate with sodium hydroxide.

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* A recently developed method for the decomposition of tantalite concentrates involves treatment with NaOH solutions at 200° in autoclaves; this provides a high degree of decomposition and reduces the hydroxide consumption by a factor of three as compared with the fusion method /24/.

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Fusion and aqueous processing of the melt. Assuming that ortho salts are the only salts formed, the processes occurring during the fusion may be approximately described by the following equations:

$$Fe(TaO_3)_2 + 6NaOH = 2Na_3TaO_4 + FeO + 3H_2O;$$
$$Fe(NbO_3)_2 + 6NaOH = 2Na_3NbO_4 + FeO + 3H_2O.$$

Similar equations can be written for $Mn(TaO_3)_2$ *and* $Mn(NbO_3)_2$.

The ortho salts undergo hydrolytic decomposition during the aqueous processing of the melt:

$$Na_3TaO_4 + 30H_2O = 4Na_2O \cdot 3Ta_2O_5 \cdot 25H_2O + 10NaOH;$$
$$12Na_3NbO_4 + 43H_2O = 7Na_2O \cdot 6Nb_2O_5 \cdot 32H_2O + 22NaOH.$$

It must be taken into account that in addition to FeO and MnO, Fe_2O_3 and Mn_3O_4 are also formed during fusion, since the oxygen present in the melt causes partial oxidation of the divalent iron and manganese to higher valency compounds. The ferric iron is present in the melt as ferrite, $Na_2O \cdot Fe_2O_3$. Ferrite decomposes during aqueous treatment according to the equation:

$$Na_2O \cdot Fe_2O_3 + H_2O = 2NaOH + Fe_2O_3.$$

During fusion, most of the manganese may be oxidized to the manganate Na_2MnO_4, which is dissolved during aqueous processing, the manganate coloring the solution green.

The impurity elements, silicon (SiO_2), tin (SnO_2), tungsten (as wolframite), aluminum (Al_2O_3 and aluminosilicates) form the soluble sodium salts, Na_2SiO_3, Na_2SnO_3, Na_2WO_4, and $NaAlO_2$ during fusion with sodium hydroxide. The titanium, present as an impurity in the form of the minerals rutile or ilmenite, forms sodium titanate Na_2TiO_3 or possibly $Na_2Ti_2O_5$ during the fusion, which is insoluble in water and which remains in the precipitate together with the niobium and tantalum.

The solubility of sodium tantalate and niobate in water drops sharply in the presence of free alkali or, rather, in the presence of an excess of sodium ions in the solutions. Thus, the solubility of sodium niobate ($7Na_2O \cdot 6Nb_2O_3 \cdot 32H_2O$) in a 1% solution of NaOH at 90° is 1.1 g/l, while in water it is 26 g/l, i. e., 20 times higher. Hence, a certain level of free alkali in the solution must be maintained in order to reduce to a minimum dissolution of niobium and tantalum during aqueous processing of the melt. In practice, aqueous treatment is carried out at NaOH concentrations of at least 5%.

The fusion of tantalite or columbite concentrates with sodium hydroxide is carried out in iron crucibles which are placed in gas-fired or electrical (shaft) furnaces. The approximate consumption of alkali is 300 kg per 100 kg of concentrate.

The first operation involves fusion of the total amount of sodium hydroxide, (or sodium hydroxide containing 10% soda ash which is added in order to reduce the melting point and the viscosity of the melt) at about 400°. The melt is then stirred continuously with steel rods, and the concentrate, crushed to a particle size of 0.1 mm, (a smaller particle size results in increased dust-entrainment) is gradually added. As new

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portions of the concentrate are added, the temperature of the furnace is gradually increased to 800°. This is necessary in order to keep the melt liquid. The melt is held for 20 to 30 minutes at the maximum temperature and is then poured directly into water; safety measures must be taken, as contact of the alkali with the skin may cause serious burns.

The aqueous processing is carried out at a solid : liquid ratio of 1 : 3 or somewhat higher. A concentrated alkaline solution is formed in the first stage of the processing; this solution contains the bulk of the impurities — silicon, tin, tungsten, aluminum, sulfur, and phosphorus — in the form of water-soluble sodium salts. The dark-brown precipitate contains sodium niobates and tantalates as well as iron and manganese oxides and hydroxides and sodium titanate.

The precipitate is allowed to settle, the solution is separated by decantation, and the precipitate is washed several times with hot water containing about 5% NaOH, which is added in order to prevent the dissolution of niobium and tantalum.

Digestion of the precipitate with acid. The precipitate is decomposed by heating with hydrochloric acid. Sodium niobate and tantalate are converted into the hydrated oxides:

$$4Na_2O \cdot 3Ta_2O_5 + 8HCl + (x-4)H_2O = 3Ta_2O_5 \cdot xH_2O + 8NaCl;$$
$$7Na_2O \cdot 6Nb_2O_5 + 14HCl + (x-7)H_2O = 6Nb_2O_5 \cdot xH_2O + 14NaCl$$

Iron and manganese oxides dissolve in the acid, yielding the respective chlorides. Chlorine is evolved as a result of the reduction of manganese from higher valency states to manganous compounds:

$$Mn_3O_4 + 8HCl = 3MnCl_2 + Cl_2 + 4H_2O.$$

When the cake is treated with hydrochloric acid, sodium titanate is converted to titanic acid H_2TiO_3, which is partially dissolved. The bulk of the titanium remains in the precipitate together with niobium and tantalum oxides.

Digestion with ~ 20% hydrochloric acid is carried out in rubber-lined iron vessels or earthenware tanks heated by superheated steam. When the decomposition is completed, the color of the dark-brown precipitate turns white, which is the color of the niobium and tantalum oxides, while the color of the solution turns dark-yellow as a result of the presence of iron and manganese chlorides. The finely dispersed precipitate of hydrated pentoxides is difficult to separate by filtration. The precipitate is rinsed with hot water, acidified with hydrochloric acid, in order to remove the iron and manganese salts, and the solution is separated by decantation. The rinsed precipitate is separated by filtration while still hot. The precipitate, consisting of the hydrated pentoxides, is dried at 100 to 120°. The powder obtained after drying still contains 20 to 25% H_2O.

The approximate composition of the oxide mixture obtained by the above method is: 96 to 99% $(Ta, Nb)_2O_5$, 0.1 to 0.5% SnO_2, up to 0.5% SiO_2, 0.5 to 1.0% TiO_2, up to 1% FeO+MnO, on the dry, water-free product.

The oxide mixture is subsequently converted into pure compounds.

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26. PROCESSING OF TANTALITE-COLUMBITE BY FUSION WITH POTASSIUM HYDROXIDE /4/

Fusion with potassium hydroxide is expedient if it is desired to produce a purer mixture of tantalum and niobium oxides. When the concentrate is fused with potassium hydroxide (in the same way as the fusion with sodium hydroxide described above), the minerals tantalite and columbite are decomposed, and water-soluble potassium tantalate and niobate, as well as iron and manganese oxides, are formed. The main impurities (silica, cassiterite, wolframite, and titanium minerals) react to yield the potassium salts of silicic, stannic, tungstic, and titanic acids.

When the melt is leached with water, K_2SiO_3, K_2WO_4, K_2SnO_3, and $KAlO_2$ are dissolved together with niobium and tantalum. Although K_2TiO_2 is a sparingly soluble salt, a fraction of the titanium dissolves in the presence of tantalum and especially niobium; this is attributed to the formation of complex titanium-tantalum or titanium-niobium compounds. The alkaline solution is then treated with sodium chloride or sodium hydroxide, and the sparingly soluble sodium tantalate and niobate are precipitated. The silicon, tungsten, tin, and aluminum present as impurities remain in the solution. The precipitate, consisting of sodium tantalate and niobate is digested with acids, and a mixture of tantalum and niobium oxides with a very low impurity content is obtained.

When the above method was used a concentrate containing 44% Ta_2O_5, 16.1% Nb_2O_5, 6.5% TiO_2, 9.9% SiO_2, 6.1% FeO, 5.3% MnO, 4.4% SnO_2, 3.7% Al_2O_3 and 0.2% WO_3 yielded a mixture of tantalum and niobium pentoxides containing 99.22% $Ta_2O_5 + Nb_2O_5$, 0.36% TiO_2, 0.01% Fe_2O_3 and traces of SnO_2. The compounds SiO_2 and MnO were not found in the mixture.

A pentoxide mixture of the above composition can be used for the production of tantalum-niobium alloys by thermal reduction with carbon or by electrolysis (see below).

27. DECOMPOSITION OF TANTALITE-COLUMBITE WITH HYDROFLUORIC ACID /1, 2/

The finely-divided tantalite (columbite) is decomposed with hot concentrated hydrofluoric acid. The main decomposition reactions are:

$$Fe(RO_3)_2 + 16HF \rightarrow 2H_2RF_7 + FeF_2 + 6H_2O;$$
$$Mn(RO_3)_2 + 16HF \rightarrow 2H_2RF_7 + MnF_2 + 6H_2O.$$

All elements (tin, titanium, silicon, tungsten, etc.) originally present in the associated minerals are dissolved, together with niobium, tantalum, iron, and manganese.

Thus, the decomposition of concentrates by hydrofluoric acid yields solutions which are contaminated with large amounts of impurity elements, which hamper the separation of pure tantalum and niobium compounds. This is the main reason for the limited use of the above method in industrial practice. However, recently developed methods for the separation of tantalum from niobium and their isolation from other elements have shown that the decomposition of tantalite (columbite) with hydrofluoric acid as a technological process has the advantage of being much shorter (there are fewer stages) than the fusion of concentrates with alkalies.

The digestion of concentrates with hydrofluoric acid is carried out in steel tanks covered with lead and lined with graphite blocks. The stirrers may be prepared from monel metal, an alloy of nickel containing 27 to 29% copper.

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The ore concentrate, which is crushed to a particle size of about 0.074 mm, is decomposed with hot 70 to 72% HF. The acid consumption depends on the composition of the concentrate and the original mineral (the $Nb_2O_5 : Ta_2O_5$ and FeO : MnO ratios), and on the processing conditions. The consumption of 70% HF is 1.2 to 2.5 ton/ton concentrate.

In some industries, a mixture of hydrofluoric and sulfuric acids is used in order to increase the degree of decomposition of the concentrate. In most cases the pulp is heated with superheated steam, which is injected through a rubber hose. The pulp may be heated by means of electric graphite heaters.

Part of the hydrofluoric acid evaporates during the decomposition process. This requires that the apparatus be fitted with good exhausts and that the HF be absorbed in a scrubber irrigated with lime water.

Twofold processing of the concentrate is occasionally required in order to provide quantitative decomposition. When the decomposition is completed, the pulp is diluted with water. The solutions are filtered using cotton or polyvinylchloride filter tissues in rubber-lined filter-presses.

Until recently, tantalum and niobium were isolated from the hydrofluoric acid solutions in the form of the fluoride complexes, K_2TaF_7 and $K_2NbOF_5 \cdot H_2O$, by a method which is described below. At present tantalum and niobium are extracted from these solutions by selective extraction with organic solvents. The nature of the extraction process is discussed in Section 29.

28. PROCESSING OF TITANIUM-NIOBIUM CONCENTRATES /5, 7, 18/

The case of loparite concentrates will be examined as an illustrative example of the processing technology of complex titanium-tantalum-niobium raw materials containing lanthanides. Loparite concentrates contain 8 to 9% $(Nb + Ta)_2O_5$ (with a $Nb_2O_5 : Ta_2O_5$ ratio of about 14 : 1), 32 to 35% TiO_2, and 26 to 28% $(Ce, La...)_2O_3$.

Loparite may be decomposed with inorganic acids (concentrated sulfuric acid, hydrofluoric acid). However, the resulting solutions have a complex composition and the isolation of individual valuable components is complicated. Particular difficulties are encountered in the separation of titanium from niobium and tantalum.

Chlorination is the simplest method for the extraction of all valuable components from loparite. This method involves treatment of the ore concentrate with chlorine gas at 750 to 850°. Differences in the volatility of the chlorides formed permit separation of the main components of the concentrate. The tantalum, niobium, and titanium chlorides which have relatively low boiling points (see Table 21) are volatilized and entrained with the gaseous phase and trapped in special condensers; the lanthanide, sodium, and calcium chlorides, which have high boiling points, remain in the furnace residue.

A flow sheet of the chlorination of loparite concentrate is shown in Figure 54.

The chlorination of the stable oxygen-containing compounds is usually carried out in the presence of a reducing agent (coke), which permits processing at 750 to 850°.

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TABLE 21

Melting and boiling points of certain chlorides

Chloride	Temperature, °C		Chloride	Temperature, °C	
	melting	boiling		melting	boiling
$NbCl_5$	204.7	248.3	Al_2Cl_6	Sublimes	180
$NbOCl_3$	Sublimes	~ 400 (sublimes)	$SiCl_4$	-67	58
			$CeCl_3$	800	1730
$TaCl_5$	216.5	234	$LaCl_3$	850	1750
$TiCl_4$	-23	136	$CaCl_2$	782	2027
$FeCl_3$	304	319	NaCl	800	1465

The main chlorination reactions are as follows:

$$Nb_2O_5 + 3Cl_2 + 3C = 2NbOCl_3 + 3CO;$$
$$Nb_2O_5 + 5Cl_2 + 5C = 2NbCl_5 + 5CO;$$
$$Ta_2O_5 + 5Cl_2 + 5C = 2TaCl_5 + 5CO;$$
$$TiO_2 + 2Cl_2 + 2C = TiCl_4 + 2CO;$$
$$Ce_2O_3 + 3Cl_2 + 3C = 2CeCl_3 + 3CO.$$

These reactions also yield CO_2 and smaller amounts of phosgene ($COCl_2$). The phosgene may chlorinate the oxides.

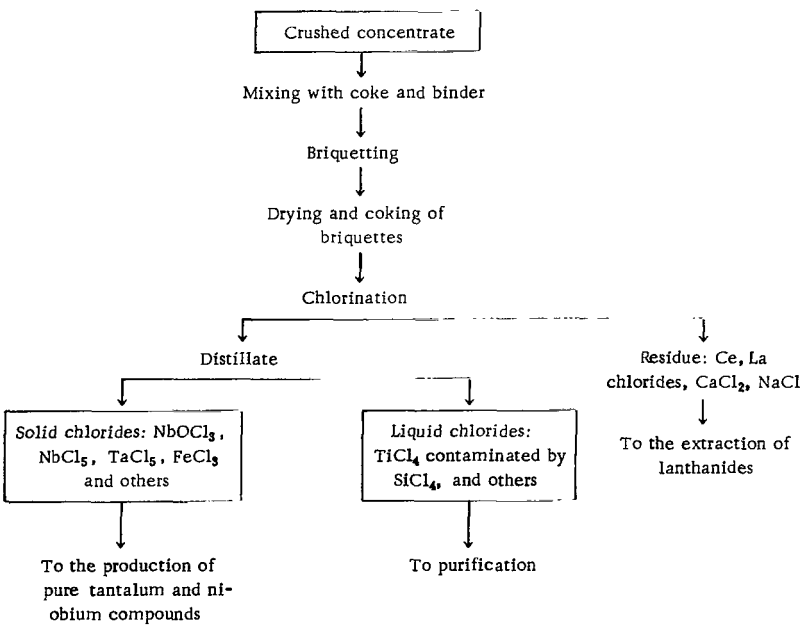

FIGURE 54. Processing of loparite concentrates by the chlorination method.

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The $CO : CO_2$ ratio in the gases depends on the temperature and the chlorination conditions. Carbon monoxide is the main component of the gaseous phase at temperatures between 750 and 850°. The chlorination is carried out in shaft furnaces, and the charge is briquetted.

Mixing, briquetting, and coking. Petroleum coke is used as the reducing agent; the amount taken is determined experimentally, and fluctuates between 20 and 30%.

The crushed concentrate and coke (particle size 0.177 to 0.15 mm) are mixed in the required ratio in screw-type, paddle or other type blenders. A binder is added to the mixture before briquetting; petroleum or coal pitch, resins, and some other materials are used as binders.

Roller presses are the most convenient briquetting equipment. They consist of two rollers rotating in opposite directions and fitted with belt-type formers with egg-shaped or pillow-like cavities (Figure 55).

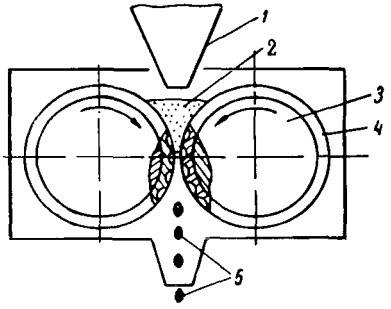

FIGURE 55. Roller press for briquetting.

1 — bin; 2 — mixture for briquetting; 3 — rollers; 4 — roller belt with egg-shaped cavities; 5 — briquettes.

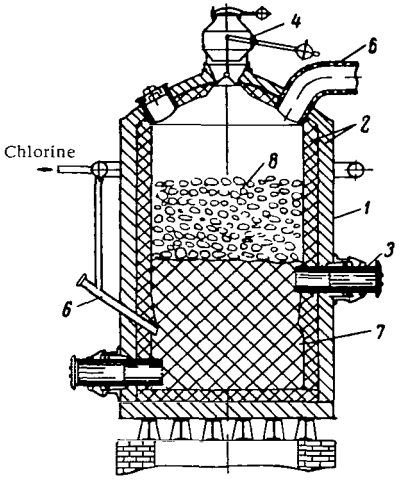

FIGURE 56. Electrical shaft furnace for the chlorination process.

1 — jacket made of steel sheets; 2 — lining; 3 — carbon electrodes; 4 — feed device; 5 — steam-gas mixture outlet; 6 — tuyeres (for chlorine supply); 7 — packing (carbon cylinders); 8 — briquetting charge.

The charge on the rotating rollers is fed from the top and fills the former cavities. Pressing is done at about 150 to 300 kg/cm^2. When pitch or resin are used as binders the mixture is heated by means of steam fed to the steam jacket of the blender, to 80 to 120° before pressing in order to soften the binder. The approximate size of the pellet-shaped briquetts is 50×40×35 mm.

The briquettes are coked, i. e., heated to 700 to 800° in the absence of air in order to increase their strength, to expell the volatile components and to increase their porosity (gas permeability).

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The coking is carried out in batch or continuous retort furnaces.

Chlorination. The chlorination of the briquettes is usually carried out in electrical shaft furnaces (Figure 56) with an internal diameter of the shaft of about 4.5 to 6 m and a height of up to 8 m. The furnace is lined with dense chamotte or Dinas bricks. The lower part of the furnace contains two rows of carbon electrodes. There are three electrodes in each row, at an angle of 120°. The space between the electrodes is packed with carbon rods, which serve as an electrical resistor which maintains the required temperature in the furnance. A voltage of 60 to 100 V is applied to the electodes, the voltage being reduced as the packing heats up.

The briquettes are charged into the furnace through a hermetically-sealed charging device. They fill a part of the furnace space over the packing. By controlling the level of the raw material in the furnace and the rate of supply of chlorine, the process may be carried out at the expense of the heat of the chlorination and the supply of heat may be shut off or considerably reduced.

The chlorine coming from storage tanks, which are usually located in a special basement, passes through a chlorine-supply line and is fed to the furnace through tuyeres placed below the upper row of electrodes.

The variables which must be controlled during the operation of the furnace are: the rate of supply of chlorine, the gas pressure in the furnace, the temperature, and composition of the exhaust gases.

The vapor-gas mixture containing volatile niobium, tantalum, titanium, iron, silicon and aluminum chlorides passes through a tube at the top of the furnace into a series of condensers (Figure 57). Solid niobium and tantalum chlorides ($NbOCl_3$, $NbCl_5$, $TaCl_5$) condense together with iron and aluminum chlorides in the first condenser which is maintained at 160 to 180°. The second condenser serves for the condensation of liquid titanium chloride. Spray condensers containing precooled liquid $TiCl_4$ are most often used for this purpose. A fraction of the niobium, tantalum and iron chlorides, entrained with the gas stream, may condense in the second condenser. Moreover, $SiCl_4$, which is soluble in liquid titanium chloride, condenses together with $TiCl_4$ (for more details see chapter on titanium). The gases from the second condenser, which may occasionally contain some chlorine and HCl vapors, are passed through a sanitary scrubber which is irrigated with lime water in order to bind the chlorine.

The nonvolatile lanthanide, calcium and sodium chlorides formed in the chlorination are fused at the process temperature (800 to 900°) and flow through the pores in the carbon packing onto the furnace bottom, from which they are periodically discharged.

Thus, the chlorination of loparite yields three products: a melt containing lanthanide chlorides, a condensate consisting of tantalum and niobium chlorides contaminated by iron, and technical titanium tetrachloride.

The purification of titanium tetrachloride will be described in the chapter "Titanium". However, we must note here that tantalum and niobium chlorides are sparingly soluble in $TiCl_4$. At 18° the solubility of $TaCl_5$ and $NbCl_5$ in $TiCl_4$ is 0.4 and 0.45% by weight respectively, and it increases in the presence of aluminum chloride. The solubility of $NbOCl_3$ and $TiCl_4$ does not exceed a few hundredths of one percent /25/.

In order to obtain a mixture of tantalum and niobium oxides, the chloride condensate is subjected to hydrolytic decomposition in a hydrochloric acid solution:

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$$2NbOCl_3 + (x+3)H_2O \rightarrow Nb_2O_5 \cdot xH_2O + 6HCl;$$
$$2TaCl_5 + (x+5)H_2O \rightarrow Ta_2O_5 \cdot xH_2O + 10HCl.$$

Under certain conditions, which must be determined in each case, the hydrolysis can be carried out so as to ensure that the concentration of iron in the tantalum and niobium hydroxides is reduced to a negligible value. The hydrolysis also causes partial separation of titanium, which is present as an impurity. The resulting mixture of hydroxides (up to 80% $(Nb,Ta)_2O_5$, 1.5 to 3% TiO_2, 3 to 7% Fe_2O_3 and 0.5 to 2% SiO_2) is then forwarded to the purification stage and the separation of tantalum and niobium is then carried out.

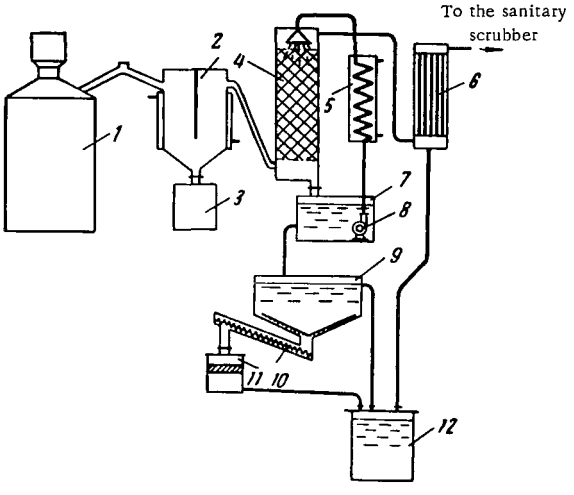

FIGURE 57. Installation for the chlorination of titanium-tantalum-niobium concentrates.

1—furnace (chlorinator); 2—condenser for trapping niobium and tantalum chlorides; 3—container for solid chlorides; 4—spray condenser; 5—cooler for the titanium chloride which is returned for spraying; 6—condenser; 7—container for titanium chloride; 8—pump; 9—thickener; 10—conveyer for the supply of slurries; 11—filter; 12—container for technical grade titanium chloride.

29. SEPARATION OF TANTALUM AND NIOBIUM AND PURIFICATION OF THEIR COMPOUNDS

Because of the similar properties of their chemical compounds, the separation of tantalum from niobium is very difficult.

Two separation methods are used in industry:

1) fractional crystallization of complex fluoride salts (the Marignac process);

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2) extraction with organic solvents.

Of major interest from the industrial point of view are also separation methods based on differences in the volatilities of the chlorides (rectification methods) and the selective reduction of niobium pentachloride to lower chlorides.

Ion-exchange methods for the separation of tantalum from niobium have been developed, but their output is low and they may be used only for relatively small-scale production of pure tantalum and niobium compounds.

Removal of accompanying elements and contaminants from pure compounds usually takes place during the separation of niobium from tantalum.

Fractional crystallization of the complex fluorides

A method for the separation of tantalum and niobium, which until recently was the industrial method mainly employed for the separation of these elements, was proposed in 1865 by a Swiss chemist, Marignac.

The method is based on differences in the solubility of potassium fluotantalate K_2TaF_7 and potassium niobium oxyfluoride $K_2NbOF_5 \cdot H_2O$. The separation is further facilitated by the different crystalline structure of these salts.

The separation of tantalum and niobium was greatly simplified as a result of studies carried out in the Soviet Union, which permitted the processing mechanism to be scientifically understood.

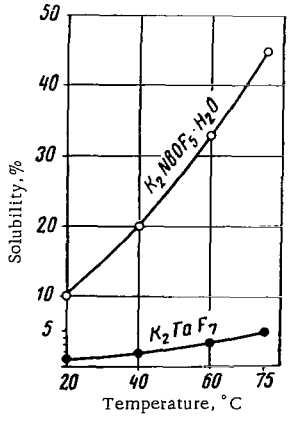

FIGURE 58. Solubility of potassium niobium oxyfluoride and potassium fluotantalate in 1% HF.

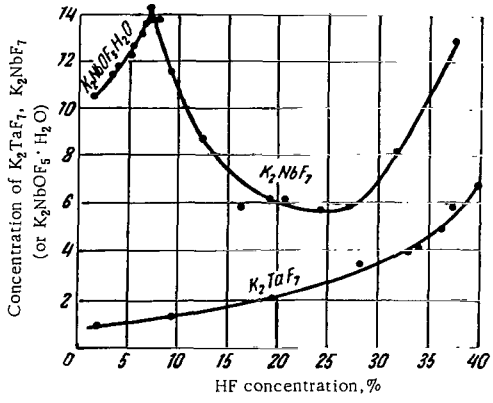

FIGURE 59. Solubility of the complex tantalum and niobium fluorides in hydrofluoric acid at 25° as a function of the acid concentration.

Curves, based on the data of Meerson, Zverev, and Zubkova on the solubilities of potassium fluotantalate and potassium niobium oxyfluoride in 1% HF at 20 to 75° are presented in Figure 58. Within the temperature range mentioned, the solubility of the niobium salt is 10 to 12 times that of the tantalum salt /10/.

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Curves based on the data of Savchenko and Tananaev /11/ on the solubilities of the complex tantalum and niobium fluorides at 25° as a function of the HF concentration are presented in Figure 59.

The solubility isotherm of the complex niobium salts is composed of two sections. The first region of increasing solubility corresponds to the equilibrium between the solution and $K_2NbOF_5 \cdot H_2O$ in the solid, crystalline phase. The solubility of the salt increases with increasing HF concentration, to a maximum at $\sim 7\%$ HF. This increase in solubility is attributed to the increased stability of $[NbF_7]^{2-}$ ions with increasing HF concentration. As a result, part of the potassium niobium oxyfluoride is converted into potassium fluoniobate:

$$K_2NbOF_5 + 2HF \rightleftarrows K_2NbF_7 + H_2O$$

The solution becomes unsaturated with respect to $K_2NbOF_5 \cdot H_2O$ and this causes dissolution of an additional amount of the crystals. When the HF concentration reaches 7%, the solution becomes saturated with respect to both salts. This "transition point" corresponds to the common solubility of $K_2NbOF_5 \cdot H_2O$ and K_2NbF_7.

The second region in the isotherm corresponds to the equilibrium between the solution and K_2NbF_7 crystals. The solubility of the salt first decreases (to 26 to 27% HF) and then increases. The decrease in solubility is attributed to the suppression of the hydrolysis of K_2NbF_7 with increasing HF concentration. The subsequent increase in solubility at higher HF concentrations is attributed to the formation of a new ionic species $[NbF_6]^-$ according to the equation:

$$K_2NbF_7 + HF \rightleftarrows KNbF_6 + KHF_2.$$

In contrast to potassium fluoniobate, potassium fluotantalate is not hydrolyzed in solutions containing a small amount of hydrofluoric acid. As a result, the normal fluotantalate K_2TaF_7 is stable at all HF concentrations up to 45%. The solubility of K_2TaF_7 increases with increasing HF concentration.

A comparison between the solubility curves of the tantalum and niobium salts (Figure 59) shows that the fractional crystallization of tantalum and niobium is conducted most conveniently at HF concentrations between 1 and 7%. This is the concentration range in which $K_2NbOF_5 \cdot H_2O$ is the stable form of niobium, and the difference in the solubilities of the tantalum and niobium salts is the greatest.

The solubility of the complex niobium and especially tantalum salt is greatly affected by excess potassium fluoride added to the solution. The solubility of K_2TaF_7 drops by a factor of 10, 15 to 20, and 35 as the excess concentration of KF reaches 1, 2, and 5% respectively (Figure 60). In the case of the niobium salt, increasing the KF concentration to 5% causes a drop in the solubility of the salt by a factor of 2 to 3 /11/.

The solubility of tantalum salts drops sharply in the presence of niobium salts (Figure 61). The presence of the niobium salt leads to the creation of an excess of potassium and fluoride ions, which reduces the solubility of the tantalum salt. Thus, the solubility of K_2TaF_7 drops to 0.05% at a niobium salt concentration of 1.5 to 1.7% (at 20°) or 3.5 to 3.7% (at 60°).

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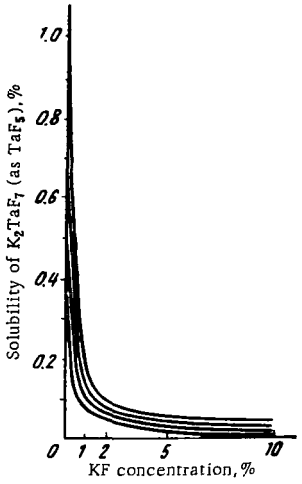

FIGURE 60. Variation of the solubility of K_2TaF_7 with KF concentration. Upper curve — solution containing 1% HF; lower curve — 5% HF.

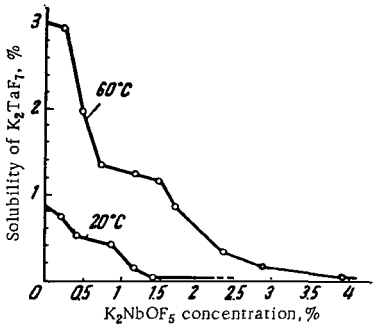

FIGURE 61. Variation of the solubility of K_2TaF_7 with K_2NbOF_5 concentration.

A flow sheet of the production of the complex tantalum and niobium salts is shown in Figure 62.

Moist tantalum and niobium oxides, or tantalum and niobium oxides dried at 100 to 120°, are dissolved in concentrated (35 to 40%) hydrofluoric acid; an excess of HF is taken over the stoichiometric amount required for the reactions:

$$Ta_2O_5 + 14HF = 2H_2[TaF_7] + 5H_2O;$$
$$Nb_2O_5 + 10HF = 2H_2[NbOF_5] + 3H_2O.$$

The dissolution is carried out in rubber-lined or lead-lined vessels at 70 to 80°. The liquid is allowed to settle and the clear solution is separated by decantation and filtered through cotton or polyvinylchloride filters.

The volume of the solution is so adjusted that after the subsequent addition of the potassium salt the concentration of K_2NbOF_5 reaches 3 to 6%. This is below the solubility limit for that salt. Simultaneously, the concentration of free HF is reduced to 1 to 2%, which facilitates subsequent operations. A potassium salt (KCl and occasionally K_2CO_3) is added to the hot dilute solution, in the amount required for the formation of K_2NbOF_5 and K_2TaF_7 when complex fluorides are formed in the reactions:

$$H_2[TaF_7] + 2KCl + K_2[TaF_7] + 2HCl;$$
$$H_2[NbOF_5] + 2KCl = K_2[NbOF_5] + 2HCl.$$

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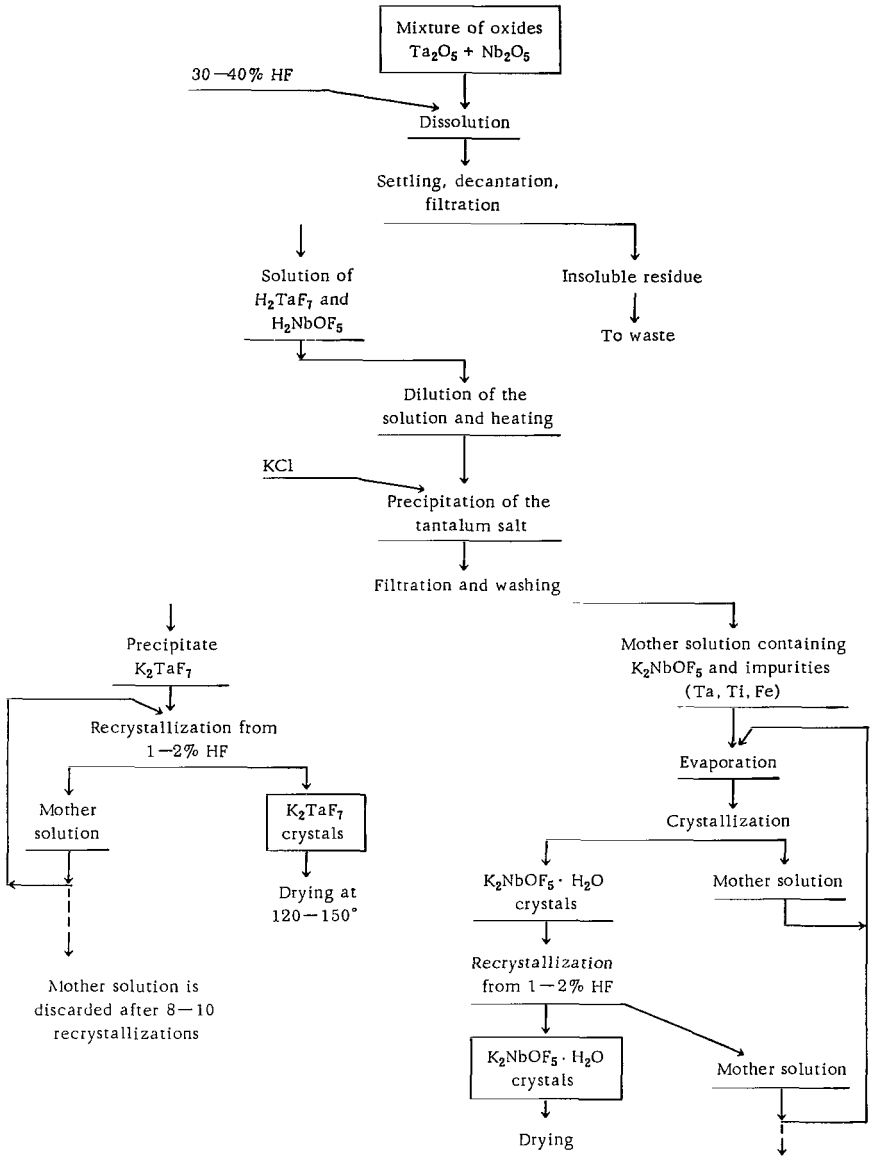

FIGURE 62. Flow sheet of the separation of tantalum and niobium by fractional crystallization of their complex fluoride salts.

The hydrochloric acid formed in the reaction has little effect on the ratio of the solubilities of potassium fluotantalate and potassium niobium oxyfluoride. Potassium fluoride is not commonly used in practice since it is expensive and difficult to handle (very hygroscopic).

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The tantalum salt separates out of solution in the form of needle-shaped crystals, which are separated by filtration after allowing the solution to cool. Silicon in the form of K_2SiF_6 is precipitated quantitatively with the tantalum salt. The precipitate also contains up to 50% of the titanium and a small fraction of the niobium (5 to 6% of the amount initially present in the solution) in the form of complex fluoride salts.

An additional purification stage involves the recrystallization of K_2TaF_7 from 1 to 2% HF. The potassium fluotantalate produced contains 0.1 to 0.3% niobium. The silicon content reaches $\sim 0.3\%$, that of iron $\sim 0.2\%$, and that of titanium 0.01 to 0.02%. The mother solution is evaporated. The compound $K_2NbOF_5 \cdot H_2O$ crystallizes after the solution is cooled, and is then purified by recrystallization.

Titanium, which is always present as an impurity in the mixture of tantalum and niobium oxides, forms the salt $K_2TiF_6 \cdot H_2O$, which is isomorphous with the niobium salt $K_2NbOF_5 \cdot H_2O$. At 20° the solubility of the titanium salt is about 12 g/l, which is lower than the solubility of the niobium salt (about 100 g/l). Since the salts are isomorphous, the titanium salt crystallizes out together with the niobium salt. As a result, the niobium salt always contains titanium, which is removed only partially in the recrystallization of the niobium salt. The niobium salt produced by crystallization of potassium niobium oxyfluoride also contains some tantalum (0.5—2%).

The method yields a pure tantalum salt, but it is difficult to produce a niobium salt of sufficient purity. The niobium salt is usually contaminated with titanium, silicon, and tantalum. This is the main disadvantage of the Marignac process.

The extraction method

The fundamentals of extraction. Extraction processes have lately found extensive use in the hydrometallurgy of the nonferrous and rare metals. These processes are based on the selective extraction of the compounds of a given element from an aqueous solution into an organic solvent which is immiscible with water.

When the aqueous solution and the organic solvent are brought into contact, the substances present in the aqueous phase are distributed between the two phases. An equilibrium state is established after a certain time. The equilibrium distribution of a substance is characterized by the distribution coefficient, i.e., by the ratio of the equilibrium concentrations in the organic and aqueous phases: $\alpha = \frac{C_{org}}{C_{aq}}$.

The distribution coefficient depends on the properties of the solvent, the concentration of the extracted substance in the aqueous solution, the presence of other substances, the acidity of the solution, and the temperature. Undissociated molecules are usually extracted from the aqueous phase into the organic solvent. Hence, weak electrolytes are extracted to a higher degree. In order to depress the dissociation of salts in the aqueous solution, a large excess of an acid or a salt with the same anion as that of the extracted salt is added to the aqueous solution.

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When a solution contains simultaneously the compounds of two elements, the distribution of each element between the aqueous and organic phase will correspond to the values of their distribution coefficients.

The ratio of the distribution coefficients of two elements is known as the separation coefficient: $\beta = \frac{\alpha_1}{\alpha_2}$. This coefficient determines the effectiveness of the separation of a given pair of elements by extractive methods. It shows the change in the ratio of the concentrations of elements undergoing separation in the extract (the organic solvent) as compared with the initial ratio in the aqueous solution.

Various organic solvents — esters, ketones, alcohols, amines, hydrocarbons — are used as extractants.

The extractant must possess a high extractive capacity with respect to the substance to be extracted, and must be easily regenerated. Its solubility in water must be small to reduce losses. In order to obtain good phase separation after the mixing, it is necessary that the density of the extractant be smaller than that of water, and that the viscosity of the extractant be low. Moreover, for safety reasons, the extractant should be of low volatility and flammability, and should be non-toxic. Its stability in inorganic acids is also of importance. The cost of the extractant must also be considered.

Extraction processes are mainly carried out in two types of equipment: columns and mixer-settlers.

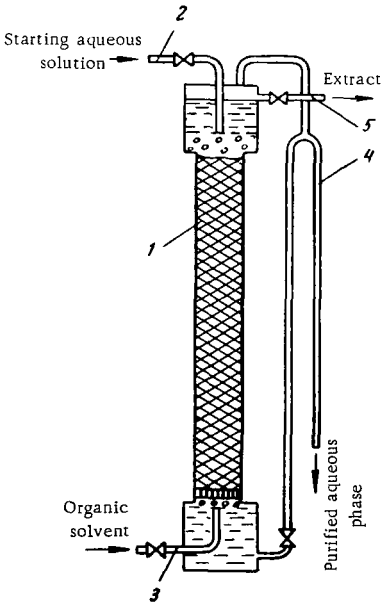

FIGURE 63. Diagram of a packed extraction column.

1—packed column; 2—input of the starting solution; 3—input of the organic solvent; 4—siphon for the discharge of the aqueous solution; 5—extract efflux.

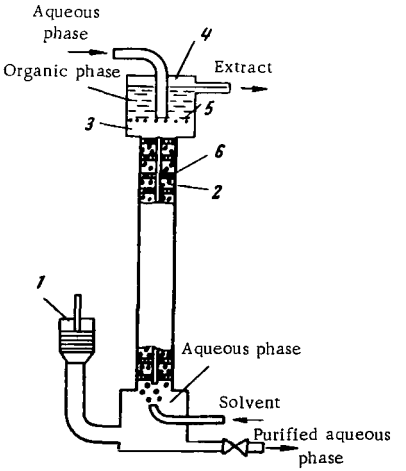

FIGURE 64. Diagram of a pulsating tray column for extraction processes.

1—pulse-generator; 2—perforated-tray column; 3—phase-separation section; 4—organic phase level; 5—interphase area; 6—perforated tray.

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In extraction columns there is a countercurrent motion of the aqueous solution and the organic solvent. In order to increase the phase-contact area, the column is packed (e.g., with rings) or else contains a number of perforated trays (tray columns).

A diagram of a packed extraction column is shown in Figure 63. Since the organic phase is lighter, it is usually fed in at the bottom of the column, while the aqueous phase is fed in at the top. The upper part of the column is not packed and serves for phase separation and for withdrawal of the organic extract. The aqueous phase is discharged from the bottom of the column through a siphon, which serves to maintain a constant level of the aqueous phase in the column.

The countercurrent motion of the liquids in packed or tray columns is a result of gravity forces alone. Thus, such columns may be used only in cases in which there is a sufficiently large difference between the densities of the aqueous and organic phases.

The effectiveness of packed or perforated-tray columns is considerably increased if the liquid currents in the column are pulsated by means of piston pumps or other devices.

In perforated-tray (hole diameter = 2—3 mm) pulsating columns (Figure 64) an upward pulse forces the organic phase through the perforations and makes it rise towards the upper tray. A downward pulse forces the aqueous phase through the perforations in a downward direction. Thus, the pulsation provides a countercurrent motion of the phases along the column and their dispersion. The pulsations in packed and tray columns increase their output approximately by a factor of three.

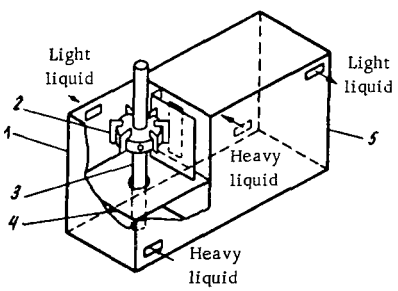

FIGURE 65. Extractor of the mixer-settler type.

1—mixing chamber; 2—turbine; 3—hollow shaft; 4—partition; 5—settling chamber.

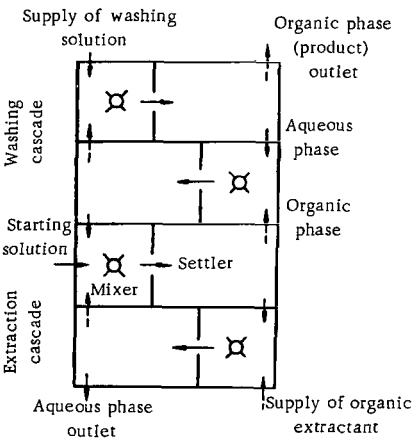

FIGURE 66. Flow sheet of continuous countercurrent extraction in a cascade of mixer-settler cells (view from the top).

Mixer-settlers are extensively used in extraction processes. They consist of a chamber for the mixing of phases with the aid of stirrers (or mixing pumps) and a settling chamber.

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A cell of a well-known mixer-settler extractor with a mixing pump is shown in Figure 65. The cell consists of mixing and a settling chambers separated by a partition. The cells are connected together forming a cascade of mixer-settlers (Figure 66). The mixing chamber is fitted with a small turbine rotating on a shaft, which ensures a rapid mixing of the aqueous and organic phases, the transfer of phases between adjacent cells, and level control of the liquid phases.

The mixer is separated into two sections by a horizontal partition. The hollow shaft of the turbine passes through an opening in the horizontal partition. The turbine pumps the aqueous solution (i. e., the heavy phase) through the hollow shaft from the lower to the upper section, dispersing the liquid through openings between the blades, where it is mixed with the organic solvent (the light phase) which is fed to the upper section of the mixing chamber.

A constant level between the aqueous (heavy) phase and the phase mixture in the lower section is maintained automatically. This is explained by the fact that the liquid is aspired by the turbine at a certain level. Thus, when the output of the turbine exceeds the rate of flow of liquid, the phase mixture is pumped from the upper to the lower chamber until a regular flow of the liquid is established.

The level of the phase mixture in the upper chamber (i. e., the level of the interface between the phase mixture and the air) gradually decreases from cell to cell in the cascade, in the streaming direction of the light phase. The phase mixture flows by gravity through the partition and into the settling chamber in which the phases separate. The light phase passes through an opening in the upper part of the settling chamber into the mixing chamber of the preceding cell while the heavy phase passes through an opening near the bottom of the chamber into the lower section of the mixing chamber of the following cell.

Thus, the flow of the heavy phase in one direction of the cascade is forced by the turbine, while the flow of the light phase in the opposite direction is caused by the gradual decrease in the liquid level in the upper section of the mixers.

In continuous countercurrent extraction the starting aqueous solution is fed to the middle of a system of extractors of the mixer-settler type, as shown in Figure 66. In this case the system has extraction and washing sections. The organic solution entering the wash sections comes in contact with the aqueous washing solution which extracts the impurities previously removed by the solvent in the extraction section.

The extractive separation of tantalum and niobium, with simultaneous removal of other (impurity) elements is mostly carried out from solutions of tantalum and niobium fluorides, containing hydrofluoric and sulfuric acids. The solutions are obtained as a result of the decomposition of ore concentrates by hydrofluoric acid, as described above, or by dissolution of the oxides in HF.

The best extractants of those tried out are methyl isobutyl ketone and tributyl phosphate (Table 22).

Tributyl phosphate (TBP) is superior to methyl isobutyl ketone because of its relatively high boiling and flash points. It has the disadvantages of high density and viscosity. For this reason TBP is often diluted with some light inert diluent, e. g., kerosene or xylene [$C_6H_4(CH_3)_2$]. Tributyl

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phosphate forms stoichiometric complexes with the extracted compounds. Thus, the complex TBP . HF is formed with hydrofluoric acid.

Depending on the hydrofluoric acid concentration, tantalum and niobium are present in solution in the form of various complex acids: H_2TaF_7, H_2NbF_7, $HTaF_6$, $HNbF_6$, and H_2NbOF_5.

TABLE 22

Some properties of the extractants

Property	Methyl isobutyl ketone	Tributyl phosphate
Chemical formula	$CH_3-\overset{\overset{O}{\|}}{C}-C_4H_9$	$(C_4H_9O)_3PO$
Boiling point, °C	115.9	177—178 (decomposes at 289 °C)
Density	0.80	0.97
Viscosity, centipoises ..	0.546	3.45
Flash point, °C	~ 27	~145
Solubility in water, % ...	1.7 —2.2	0.6

These acids are extracted by TBP in the form of trisolvates: $H_2RF_7 \cdot 3TBP$, $HRF_6 \cdot 3TBP$ (where R is Ta or Nb) and $H_2NbOF_5 \cdot 3TBP$ /19/.

Methyl isobutyl ketone and the complex fluotantalic and fluoniobic acids form complexes of the oxonium salt type, in which the hydrogen of the acid is bound to the oxygen of the ketone:

$$\left[\begin{matrix} C_4H_9 \\ \diagdown \\ C-O-H \\ \diagup \\ CH_3 \end{matrix}\right] TaF_6^-; \quad \left[\begin{matrix} C_4H_9 \\ \diagdown \\ C-O-H \\ \diagup \\ CH_3 \end{matrix}\right]_2 TaF_7^{2-}.$$

Such oxonium salts are readily soluble in excess organic solvent.

In the extraction of tantalum and niobium from solutions of their fluoride complexes by TBP or methyl isobutyl ketone, the distribution coefficients are strongly affected by the hydrofluoric acid concentration. This is especially true in the case of niobium. As is evident from Figure 67, niobium is virtually not extracted from solutions containing less than 4 moles HF per liter, while the tantalum is readily extracted. This can probably be attributed to the fact that in dilute HF solutions the niobium is present as H_2NbOF_5 which is extracted to a lesser extent than is H_2NbF_7.

Tantalum and niobium may be extracted together from concentrated HF solutions, and at the same time these two metals may be separated from many accompanying elements (e. g., Fe, Mn, Ti, Sn) whose distribution coefficients are very low, especially in the presence of sulfuric acid (Table 23).

The extractive separation of tantalum and niobium usually involves three stages:

1) joint extraction of tantalum and niobium, as a means of separating these metals from the accompanying elements (Fe, Mn, Ti, Sn, Si, and others);

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2) re-extraction of niobium from the organic solvent by water;
3) re-extraction of tantalum from the solvent by water of by aqueous solutions of salts such as ammonium fluoride.

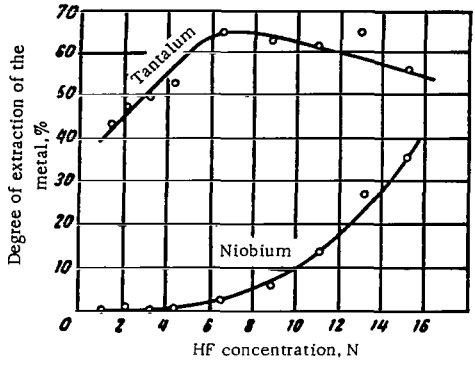

FIGURE 67. Degree of extraction by methyl isobutyl ketone of tantalum and niobium from solutions with different HF concentrations.

TABLE 23

Distribution coefficients of the ions of some elements between TBP and an aqueous solution containing 10 moles HF and 12 moles H_2SO_4 per liter

Ion and its valence	Concentration in the starting solution, g/l	$\alpha = \frac{C_{org}}{C_{aq}}$
Nb(V)	2	183
Ta(V)	2	119
Fe(III)	10	0.001
Mn(II)	2	0.017
Ti(IV)	10	0.02
Sn(IV)	2	0.05

A simplified flow sheet of the production of pure tantalum and niobium oxides from columbite concentrate, based on the extraction process used in a factory in the USA, is shown in Figure 68. The ore concentrate, crushed to a particle size of -0.074 mm, is decomposed by 70% HF with heating and stirring. The pulp is diluted to an HF content of 15 moles per liter and is filtered in a rubber-lined filter press. The clear solution is fed to the upper part of a pulsating column with perforated trays. The column and all tube joints are made of polyethylene. Methyl isobutyl ketone is fed to the lower part of the column by means of a diaphragm pump which creates a pulsating stream of the solvent.

In the column, the tantalum and the niobium are extracted by the solvent while the impurities remain in the aqueous phase. Dilute sulfuric acid is fed to the upper part of the column together with the starting solution, in order to reduce the degree of extraction of the impurities.

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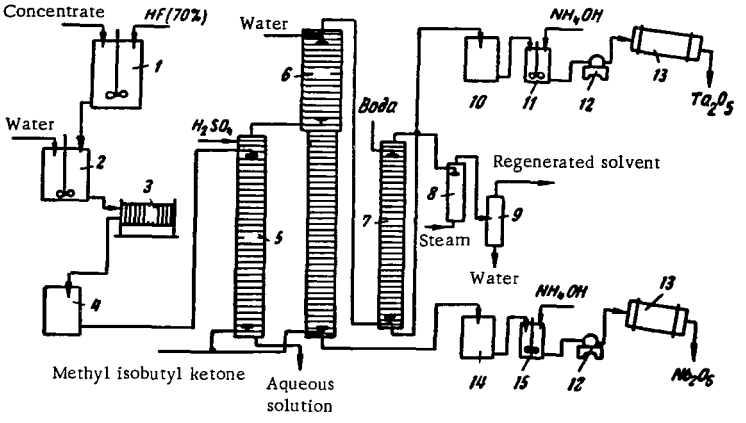

FIGURE 68. Flow sheet of the processing of columbite concentrate, including the extractive separation of tantalum and niobium:

1—reactor for the decomposition of the concentrate; 2—tank for the dilution of the pulp; 3—filter press; 4—container for the filtrate; 5—column for the joint extraction of tantalum and niobium; 6—column for the reextraction of niobium; 7—column for reextraction of tantalum; 8 and 9—apparatus for the steam distillation of the solvent; 10—collector for the tantalum solution; 11—vessel for the precipitation of Ta_2O_5; 12—filters; 13—ignition furnaces; 14—collector for the niobium solution; 15—vessel for the precipitation of Nb_2O_5.

TABLE 24

Composition of the oxides

Element	Concentration, %	
	Nb_2O_5	Ta_2O_5
Zr	< 0.05	< 0.05
Ta	< 0.03	—
Nb	—	< 0.03
F	0.06	0.06
Fe	< 0.03	< 0.01
Ti	< 0.015	< 0.015
Si	0.01	0.01
W	< 0.01	< 0.01
Ni	0.005	0.005
Cu	< 0.004	< 0.004
Al	0.002	0.002
Mg, Co, Zn, Cr, Mn, Sn, V, Mo	< 0.002	< 0.002
Cd	< 0.0005	< 0.0005
B	< 0.0001	< 0.0001

The organic solvent containing the niobium and the tantalum is fed to the middle of a pulsating column serving for the reextraction of niobium with water which is fed into the upper section of the pulsating column.

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Most of the HF from the solvent is extracted into the aqueous phase together with the niobium. At the same time, only a small fraction of the tantalum passes into the aqueous phase from which it is separated in the lower part of the column where the aqueous solution comes into contact with the upward stream of pure methyl isobutyl ketone. The aqueous solution coming from the column contains virtually only niobium. In the third column, the tantalum is extracted from the solvent by water.

After the reextraction of niobium and tantalum the solvent is purified by steam distillation and returned to the extraction cycle. The pure tantalum and niobium hydroxides are precipitated from the aqueous solutions by the addition of ammonia water. The precipitates are separated by filtration in stainless-steel vacuum filters (of the drum type) and are ignited to the oxides in drum furnaces. The concentration of impurities in the pentoxides produced by the above method is shown in Table 24.

Separation of tantalum and niobium by the chloride rectification process*

Rectification may be successfully employed in the separation of the mixture of tantalum and niobium pentachlorides, as the boiling points of the chlorides differ by 14.3° (the boiling points of $TaCl_5$ and $NbCl_5$ are 234.0 and 248.3° respectively).

The use of the rectification process for the separation of tantalum and niobium is expedient when the ore concentrates are processed by the chlorination method, yielding a condensate of tantalum and niobium chlorides, e. g., in the processing of loparite concentrates. The chlorination of the concentrate usually yields a condensate in which a large fraction of the niobium is present as the oxychloride $NbOCl_3$. Thus, additional chlorination is required in order to convert the oxychloride to the chloride.

The Soviet scientific literature contains descriptions of laboratory experiments on the rectification of tantalum and niobium chlorides in sieve-tray glass columns with a diameter of 32 to 34 mm and 25 trays, as well as larger-scale experiments in stainless-steel columns /15/.

The starting mixture of chlorides contained 80.2% Nb, 12.3% Ta, 0.3% Ti, 7.2% Fe, and 0.22% W; after rectification the yield of niobium chloride was about 60%, and it contained 0.008% Ta (on the Nb), ~ 0.005% Ti, 0.002% W, and < 0.001% Fe. About 80% Ta was obtained in the form of a concentrate containing 80%Ta (on the total amount of Ta + Nb). This concentrate, as well as other intermediate fractions, may be subjected to a second rectification in order to obtain the pure compounds.

The rectification method is characterized by a high output and a high degree of separation. It may be carried out in continuous operation columns. The pure tantalum and niobium chlorides produced may be used as the starting material for the production of tantalum and niobium (see Section 35).

Separation of tantalum and niobium by selective reduction of the chlorides

As compared with tantalum pentachloride, niobium pentachloride is more readily reduced by hydrogen (or by metals such as aluminum) to the lower chlorides. This is used as the basis of a process for the separation of tantalum and niobium. $NbCl_5$ is reduced by hydrogen at 450 — 550° to the nonvolatile trichloride:

$$NbCl_5 + H_2 \rightarrow NbCl_3 + 2HCl.$$

$TaCl_5$ is not reduced under those conditions.

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* The nature of the rectification process will be discussed in Chapter IV.

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In one variation of the method, tantalum and niobium are separated by volatilizing the $NbCl_5 + TaCl_5$ mixture at 180—200° and passing the gaseous chlorides together with hydrogen through a long tube heated to 500—550°. The $NbCl_3$ formed condenses on the walls of the tube, while the $TaCl_5$ remains in the gaseous phase and is collected in the condenser. The yield of pure $NbCl_3$ from the pentachloride has been reported to be about 70% /1/.

The difficulty of effecting the reaction as a continuous process and the necessity for repeating the process on the condensate in order to obtain pure tantalum pentachloride are among the disadvantages of the process.

Metallic niobium can be produced from the trichloride by reduction with hydrogen.

Separation of tantalum and niobium with the aid of ion exchange resins* /12/

Investigations carried out in the USSR showed that the ion-exchange separation of tantalum and niobium may be successfully effected from hydrofluoric acid solutions. It is recommended that the anion exchange resin EDE-10P, in which the active groups are (=NH) and (≡N), be used for the separation. The dynamic exchange capacity of this resin (in the Cl-form) with respect to tantalum, niobium, and titanium is 10, 7, and 5 mg-equiv/g respectively. Titanium is usually present as impurity in the solutions.

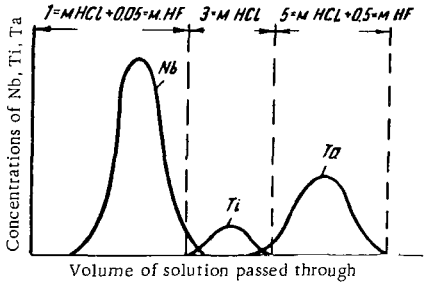

FIGURE 69. Elution curves of niobium, titanium, and tantalum sorbed on anion-exchange resin.

The affinity for the resin decreases in the order $TaF_7^{2-} > TiF_6^{2-} > NbF_7^{2-}$. Hence, in the elution of the niobium, tantalum and titanium ions sorbed in the upper layer of the resin bed, niobium is the first to be eluted, followed by titanium and tantalum. The separation effect may be enhanced by using acid solutions of various concentrations for the elution of niobium, titanium, and tantalum. For instance, niobium is eluted with a mixture of 35 g/l HCl + 1 g/l HF, titanium with HCl at a concentration of 84 g/l, and tantalum with a mixture of 180 g/l HCl + 10 g/l HF. The first fraction of the eluate contains up to 80% niobium (titanium- and tantalum-free), the

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* The fundamentals of ion-exchange chromatography method of separation of elements with similar properties will be discussed in Chapter VI.

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second fraction contains the rest of the niobium and all the titanium, and the third fraction contains pure tantalum (see Figure 69).

30. METHODS FOR THE PRODUCTION OF METALLIC TANTALUM AND NIOBIUM

Tantalum and niobium are produced by reduction of very pure compounds: oxides, complex fluoride salts, chlorides.

The industrial methods for the reduction of these compounds (which are characterized by a high stability) may be divided into three groups:

1) reduction of halides by active metals — sodium, magnesium, calcium;

2) reduction of oxides by carbon (thermal reduction with carbon);

3) electrolysis of molten salts.

Because of the high melting points of tantalum ($\sim 3000°$) and niobium ($\sim 2500°$), these metals are obtained as powders in the reduction processes. The subsequent conversion of the powders into solid, ductile metal is complicated by the fact that tantalum and niobium actively absorb gases (hydrogen, nitrogen, oxygen) which render the metals brittle. For this reason, the sintering or melting of the powders must be carried out under high vacuum, which complicates the design of the production equipment.

Of the production methods listed above, the methods based on reduction with metals are of great importance.

Such methods are known as "metallothermic". They are extensively used in the production of other rare metals (titanium, zirconium, beryllium). For this reason, we shall first discuss their theoretical principles.

31. FUNDAMENTAL PRINCIPLES OF METALLOTHERMY

Metallothermic production of metals is based on the reduction of chemical compounds (oxides, salts) by metals whose affinity for the non-metal in the compound is higher than that of the metal to be produced.

The first studies on the displacement of metals from their compounds by other metals were carried out by the Russian chemist Beketov in 1850 to 1860. These studies laid the foundations for the most common thermal reduction process — aluminothermy, which plays an important part in the modern production of ferroalloys, and in the production of a number of metals (barium, strontium, calcium) and nonferrous and rare metal alloys of technological importance.

Subsequently, silicothermy as well as magnesiothermy (mainly the production of rare metals) and thermal reduction with calcium and sodium also found wide use.

The reaction of thermal reduction by metal may be generally expressed as follows:

$$MeX + Me' \rightleftarrows Me'X + Me + Q,$$

where MeX is the compound to be reduced (oxide, halide);

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Me' is the reducing agent;
Q is the heat of reaction.

The rate and the extent of the reduction depend on the affinity of the metal acting as reducing agent and the metal in the compound to be reduced for oxygen, chlorine, fluorine, and other elements.

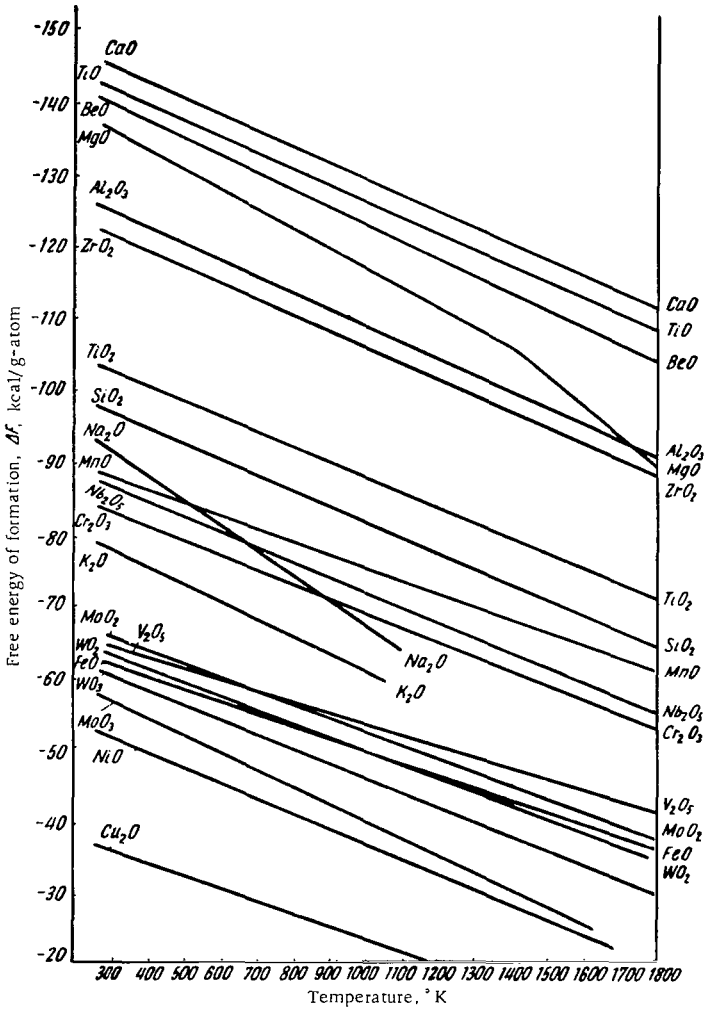

FIGURE 70. The affinity of metals for oxygen.

In many cases, the affinity of a metal for a given element may be evaluated from the heat of formation of a chemical compound from the metal and the element.

The affinity is characterized more accurately as the decrease in the free energy ΔF accompanying the formation of the compound from its elements.

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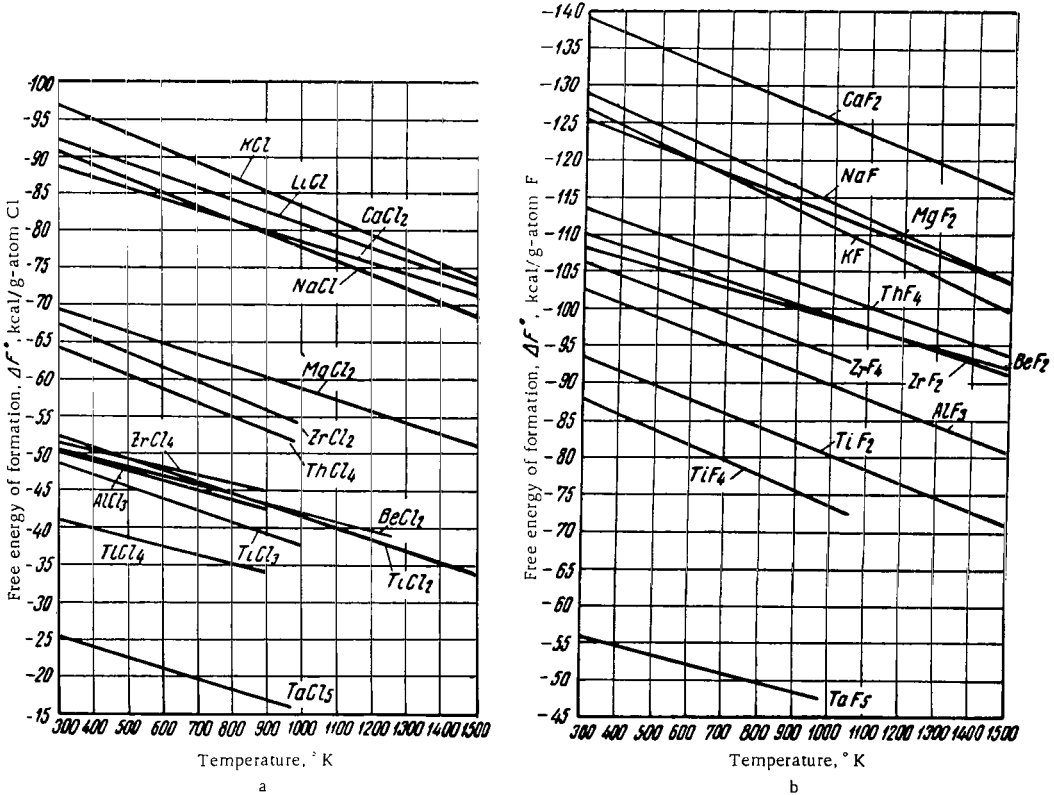

FIGURE 71. Affinity of metals for chlorine and fluorine:

a — chlorine; b — fluorine.

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The dependence of the free energy of formation of oxides and halides on the temperature is shown in Figures 70 and 71. To facilitate comparison, the values of ΔF are related to one g-atom of oxygen, chlorine, and fluorine.

A comparison of those values shows that the most active reducing agent for the rare metal oxides is calcium, followed by magnesium and aluminum; for the chlorides — sodium, calcium, magnesium; and for the fluorides — calcium, sodium, magnesium.

If one of the participants in the thermal reduction reaction displays a high vapor pressure at the temperature of the reaction, the changes in pressure may have an appreciable effect on the course of the reaction and may even reverse its direction. Thus for instance, the standard affinity of calcium for oxygen (144.3 kcal) is much higher than that of aluminum (123.8 kcal) and aluminum oxide should, therefore be reduced by calcium. However, the reduction reaction is reversible:

$$Al_2O_3 + 3Ca \rightleftarrows 3CaO + 2Al.$$

Depending on the external pressure, it may proceed in the direction of the formation of aluminum or the reduction of calcium oxide by the aluminum. The boiling points of calcium and aluminum are 1480 and 2330° respectively. When the reaction is carried out under reduced pressure, calcium (which has a lower boiling point) is expelled from the reaction zone. Under such conditions, calcium oxide is reduced by aluminum (this process is used in the production of metallic calcium). In a sealed reactor, in which vapor pressure of calcium may build up, the reaction would result in the formation of elementary aluminum.

The heat evolved in the thermal reduction by metals is often sufficient to support a spontaneous process at a high rate (the reaction must first be initiated somewhere in the mixture). In other cases the heat evolved is not sufficient to support the process and unless external heating is supplied, the reaction ceases before it can spread over the entire mixture.

In order to find out if the reduction is spontaneous or must be supported by external heating, we must know the specific heat effect q, i. e., the amount of heat required per g of the charge.

The specific heat effect of the reaction $MeX + Me' = Me + Me'X + Q$ is:

$$q = \frac{Q}{M_{MX} + A_{Me'}},$$

where M_{MeX} is the molecular weight of the compound and A_{Me} is the atomic weight of the reducing agent.

The maximum heat effect of the reaction is obtained at a stoichiometric ratio of the components in the charge. An excess or deficiency of the reducing agent diminishes the specific heat effect since a part of the material absorbs heat (heating-up, melting) without taking part in the reaction. Nevertheless, in most cases an excess of the reducing agent is required in order to obtain a higher degree of completion of the reduction.

A heating additive (activator) is added to the charge if the specific heat effect of the reaction is not sufficient to support the reaction. The activator reacts with the reducing agent with the evolution of a large amount of heat, which increases the specific heat effect.

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In other cases the heat of reaction is so high that the reaction is extremely vigorous and partial ejection of the charge (caused by the rapid expansion of gases entrapped in the pores of the charge) as well as evaporation of the reducing agent and the compounds participating in the reaction take place. In such cases the reaction is slowed down by the addition to the charge of fluxes which absorb a part of the heat, (this being consumed in the heating and melting of the flux). Fluxes are also added when a lower-melting, lower-viscosity slag is required.

The reducing agents used in thermal reduction by metals must satisfy the following requirements:

1) the reducing agent (metal) must provide for the highest possible degree of completion of the reduction at the lowest possible supply of external heat;

2) the slags formed and the excess reducing agent must be readily separated from the metallic product (by rinsing, vacuum distillation, removal of slag);

3) the reducing agent must be of high purity, in order to prevent contamination of the metal product;

4) the reducing agent must have a low solubility in the metal product and must not form chemical compounds with it;

5) the reducing agent must be readily available and reasonably cheap.

The melting and boiling points of the most common metal reducing agents and the products of thermal reduction reactions are listed in Table 25.

TABLE 25

Melting and boiling points of metallic reducing agents and their compounds

Element	Metal		Oxide	Chloride		Fluoride	
	t_{mp}	t_{bp}	t_{mp}	t_{mp}	t_{bp}	t_{mp}	t_{bp}
Na	97.7	883	1000	800	1465	992	1704
Ca	851	1480	2570	782	2027	1418	2507
Mg	650	1126	2800	714	1418	1262	2227
Al	659	2330	2045	192.4	180	1270	1272

32. PRODUCTION OF TANTALUM AND NIOBIUM POWDERS BY THERMAL REDUCTION WITH SODIUM

The thermal reduction of fluoride complexes of tantalum and niobium by sodium was the first method for the industrial production of these metals, and is still in use today. The fluoride complexes were selected as the starting compounds for this process since they are the end products in the separation of tantalum and niobium by the Marignac process.

Tantalum will be used in describing this process; until recently thermal reduction with sodium was the main process by which tantalum was produced /29/.

Because of their affinity for fluorine; sodium, calcium, and magnesium are suitable reducing agents for tantalum and niobium fluorides (see Figure 71, b). However, sodium is the only one used since the NaF formed is soluble in water and may be separated from tantalum powder

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by washing. Calcium and magnesium fluorides are sparingly soluble in water and acids. The reduction reaction

$$K_2TaF_7 + 5Na \rightarrow Ta + 5NaF + 2KF$$

is accompanied by the evolution of a large amount of heat ($\sim$ 713 kcal per kg salt and reducing agent), which is sufficient to support a self-sustained process; the charge is locally heated to 450 to 500° and the reaction spreads rapdily through the bulk of the charge. The reduction is carried out in steel crucibles in which K_2TaF_7 and Na are charged in alternate layers. The charge is covered with a layer of NaCl which forms a low-melting mixture with KF and NaF. The molten salt layer protects tantalum particles against oxidation.

The salts and the crucible must be thoroughly dried before the charging, since water vapor reacts with sodium, yielding hydrogen, which may form an explosive mixture with air in the pores of the charge. The ejection of the charge in this process is especially dangerous since it contains droplet of molten sodium. As a safeguard, the crucible is placed in a metallic casing.

The sodium bars (which are usually kept under kerosene) are cut into small pieces (special scissors are used), washed with benzene and held in the air until the benzene evaporates. The amount of sodium added to the charge is 125 — 150% of the stoichiometric.

To initiate the reaction the bottom of the crucible is heated with a blowtorch until the appearance of a red spot. The reaction spreads rapidly throughout the charge and is completed within 1 to 2 minutes. During the reaction the temperature of the charge reaches about 800 to 900°.

The metallic tantalum obtained by this process is disseminated as a fine powder within the fluoride-chloride slag containing the excess sodium metal. The molten salt is allowed to solidify and is knocked out of the crucible. The upper slag layer, which contains no metallic tantalum, is separated, the bulk of the slag is crushed into small particles in a jaw crusher and the particles are charged in small portions, with constant stirring, into the water-filled reactor. This results in the "quenching" of the metallic sodium, which reacts with water to form the hydroxide with the evolution of hydrogen.

The bulk of the salts is washed out first with cold and then with hot water and the tantalum powder is washed in porcelain tanks with dilute hydrochloric acid. The acid is used in order to obtain a more complete removal of the alkali salts and in order to dissolve the iron. To reduce the concentration of oxides, the washing with hydrochloric acid is sometimes followed by additional wash with dilute cold hydrofluoric acid. The powder is then rinsed with distilled water, isolated by filtration, and dried at 110 to 120°.

The resulting powders are of small particle size: 85% of the grains are smaller than 1μ and the rest have a particle size of 1 to 2μ. The powders contain 2 to 3% oxygen, 0.1 to 0.15% (Na+K), and about 0.15% hydrogen.

The extraction of tantalum into the powder is 92 to 94%. The losses are caused mainly by entrainment of the fine fraction of the powder with the wash water.

The same method may be used for the production of niobium metal from potassium fluoniobate /28/. To prepare K_2NbF_7 from potassium niobium oxyfluoride $K_2NbOF_5 \cdot H_2O$ (which is usually isolated from solution) the salt is recrystallized from solution containing 15 to 20% HF.

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33. PRODUCTION OF TANTALUM AND NIOBIUM BY ELECTROLYSIS

The production of metals by electrolysis is based on the cathodic reduction of the metal ions during the passage of an electric current through the electrolyte. Tantalum and niobium cannot be electrolytically separated from aqueous solutions. Like aluminum and other active metals, they can only be produced by electrolysis of molten salts.

The production of tantalum powder by electrolysis is increasingly used in industrial practice, and is about to displace the thermal reduction with sodium. This can be attributed to a number of advantages which will be discussed below.

Electrolytic methods for the production of niobium and niobium-tantalum alloys have recently been developed; in general, these methods are similar to those used in the electrolytic production of tantalum, but the efficiency of the electrolytic production of niobium is not satisfactory.

Electrolytic production of tantalum

The electrolyte used in the production of tantalum is a melt consisting of KCl, KF, and potassium fluotantalate (K_2TaF_7). Tantalum pentoxide is dissolved in the molten salts and is electrolyzed. Though it would appear more convenient to conduct the electrolysis using K_2TaF_7 alone, difficulties are caused by the so-called "anode effect". It consists in a sharp rise in the bath voltage at a certain "critical" anodic current density; this is accompanied by a drop in current intensity and the appearance of a characteristic spark discharge on the anode.

Belyaev et al., studied the causes of the anodic effect in the electrolytic production of aluminum from cryolite-alumina melts (which are in many respects similar to the melts containing K_2TaF_7 and Ta_2O_5) and established that the effect is due to insufficient wetting of the graphite by the electrolyte and, in particular, by molten fluorides /31/. The electrolyte is then separated from the surface of the anode by a film of the gases formed on the anode. The anode effect is eliminated by the addition to the electrolyte of surface active substances which improve the wetting of the graphite by the electrolyte (i. e., reduce the surface tension at the graphite-electrolyte interface).

In fact, the addition of tantalum pentoxide to the electrolyte improves the wetting of the graphite electrode by the melt and increases the critical current density associated with the appearance of the anode effect.

One recommended electrolyte composition is:

55.0% KCl, 27.5% KF, 17.5% K_2TaF_7.

The presence of potassium fluotantalate in the electrolyte is necessary in order to ensure a satisfactory solubility of tantalum pentoxide. The concentration of Ta_2O_5 in the melt commonly used in the electrolysis is 2.5 to 3% .

Whatever the true mechanism of the electrolysis, its end result is the electrolytic decomposition of tantalum pentoxide, with the separation of tantalum on the cathode and oxygen on the anode:

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$$4Ta^{5+} + 20e \rightarrow 4Ta;$$
$$10O^{2-} - 20e \rightarrow 5O_2.$$

The theoretical value of the decomposition potential of Ta_2O_5 at the electrolysis temperature (750°) is 1.65 V. It is lower than the decomposition potentials of K_2TaF_7, KCl, and KF. When using a graphite anode, the decomposition potential of Ta_2O_5 is reduced because of a secondary process occurring on the anode — the combination of oxygen and carbon with the formation of CO and CO_2, which is accompanied by a liberation of energy. Thus, the only component consumed during the electrolysis is Ta_2O_5, and the electrolyte composition remains unchanged.

The true mechanism of the electrolytic production of tantalum has not yet been finally clarified.

Investigations carried out in the USSR showed that the Ta_2O_5 added to the electrolyte reacts with K_2TaF_7 yielding the oxyfluorotantalate $K_3TaO_2F_4$. The excess K_2TaF_7 combines with potassium chloride yielding a complex salt — $K_2TaF_7 \cdot KCl$. As a result of the partial dissociation of $(TaO_2F_4)^{3-}$ and $(TaF_7)^{2-}$ anions, the melt contains Ta^{5+} cations /30/.

Discharge of the Ta^{5+} cations takes place on the cathode:

$$Ta^{5+} + 5e \rightarrow Ta.$$

The following processes may occur on the anode:

$$[TaO_2F_4]^{3-} - 4e \rightarrow [TaF_4]^{+} + O_2;$$
$$[TaF_4]^{+} + 3F^{-} \rightarrow [TaF_7]^{2-}.$$

The TaF_7^{2-} anions again react with Ta_2O_5, yielding $TaO_2F_4^{3-}$. The oxygen liberated in the process reacts with the graphite anode yielding CO and CO_2. According to the above mechanism, the oxygen migrates to the anode as $(TaO_2F_4)^{3-}$ ions.

The Ta_2O_5 content of the bath decreases in the course of the electrolysis, and the anodic effect is observed upon reaching a certain lower concentration limit; this serves as indication that a further amount of Ta_2O_5 must be added to the electrolyte.

Construction of the electrolyzer and the conditions of electrolysis

Of the electrolyzer designs which have been tried out best results were obtained when a nickel (or nickel-chromium alloy) crucible was used as the cathode, with a graphite anode placed at the center of the crucible /14/.

A diagram of such an electrolyzer is shown in Figure 72. It consists of a nichrome crucible, appliances for supporting and lifting the anode, a feeder and a heat-insulating jacket. The lower, cone-shaped part of the crucible has an opening which is closed by a stopper with a rod serving as current terminal. A hollow perforated graphite anode is placed at the center of the crucible. Tantalum pentoxide is fed into the bath through the hollow anode by means of an automatic batch feeder. This method of feeding prevents contamination of the cathodic deposit with the undissolved

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pentoxide. A flange exhauster serves to evacuate the gaseous products. The electrolyzer is supplied with a controlled direct current.

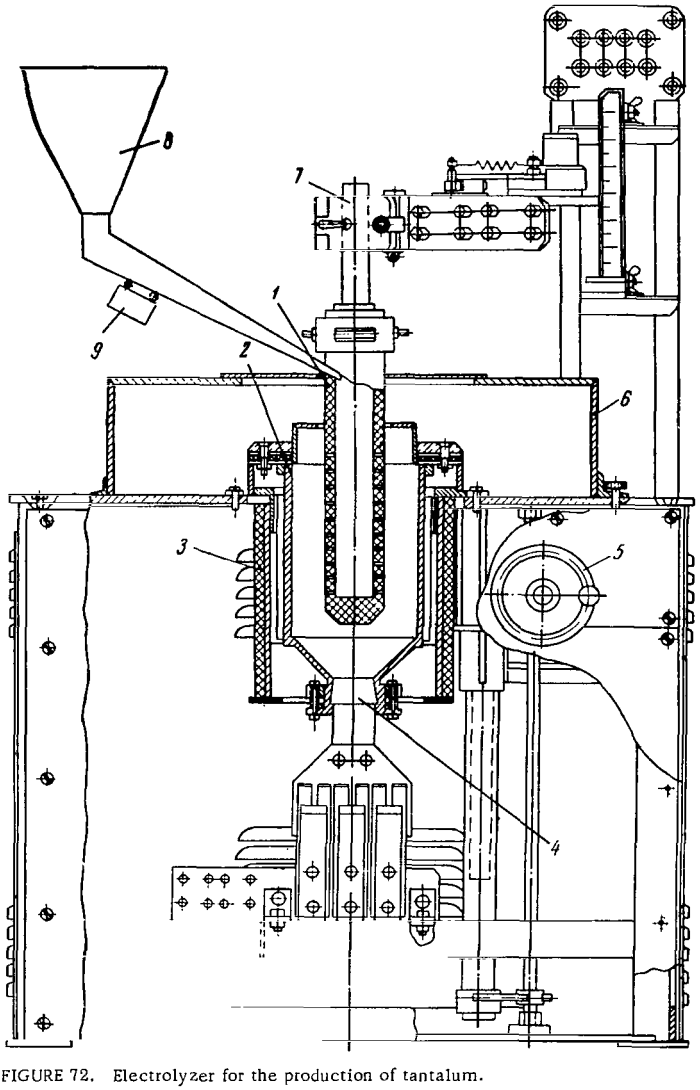

FIGURE 72. Electrolyzer for the production of tantalum.

1 — hollow graphite anode with perforated walls; 2 — nichrome crucible serving as the cathode; 3 — heat-insulating jacket; 4 — stopper with a rod serving as current terminal; 5 — control wheel for lifting the anode; 6 — cover; 7 — bracket holding the anode; 8 — feed bin for the supply of Ta_2O_5; 9 — electromagnetic vibrator for the feed bin.

The electrolysis is carried out at a cathodic current density of about 50 amp/dm^2 and an anodic current density of 120 to 160 amp/dm^2. The

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residual Ta_2O_5 concentration in the electrolyte, at which the anodic effect takes place, depends on the anodic current density. As the anodic density is increased, the anodic effect is observed at higher Ta_2O_5 concentrations in the electrolyte. The temperature of the electrolyte is maintained at 680 — 720°.

The average bath potential is determined by means of the equation:

$$E_{av} = E_{dp} + E_{el} + E_c,$$

where E_{dp} is the decomposition potential of Ta_2O_5 which, allowing for the oxidation of the graphite anode, is 1.41 V;

E_{el} is the potential drop in the electrolyte, which is equal to ρDl (ρ is the resistivity of the electrolyte, D is the current density in the electrolyte, and l is the distance between the electrodes; the value of D is taken as $D = \sqrt{d_a d_c}$, where d_a and d_c are the anodic and cathodic current densities respectively);

E_c is the potential drop in the bus bars and contacts, equal to $I\Sigma R$ where I is the current, and ΣR is the resistance of the conductors and the contacts.

In the case of a small electrolyzer designed for a current of 1000 amp and having a total crucible (cathode) volume of about 10 liters, the bath voltage is 6.5 to 7 V. In such an electrolyzer about 75% of the dissipated* electrical energy is lost as heat (heat losses through the crucible walls, from the bath and anode surfaces, and heat lost in the evaporation of the salts). The fraction of energy lost in the form of heat should decrease as the size of the bath is increased.

The initial heating and melting of the electrolyte is accomplished by shortcircuiting the electrodes (anode and cathode) with the aid of a graphite tube. When the salts are molten, the tube is taken out, tantalum pentoxide is added to the melt (to a concentration of 2.5 to 3%) and the electrolysis begun; more Ta_2O_5 is added in batches when the anode effect is observed.

Tantalum is deposited on the walls and the bottom of the crucible in the course of the electrolysis. The electrolysis is continued until about 2/3 of the useful volume of the crucible is filled with the cathodic deposit. Since a part of the electrolyte evaporates during the electrolysis, a constant level of the melt in the bath is maintained by periodic addition of a salt mixture having the same composition as the initial charge in the crucible.

When the electrolysis is completed, the anode is taken out and the electrolyte together with the cathodic deposit are cooled.

Under these electrolysis conditions, the current efficiency is about 80%, and the consumption of electrical power is about 2300 kwh per ton of tantalum.

Processing of the cathodic product

There are two methods for processing the cathodic product, their aim being to separate the electrolyte from the tantalum powder particles: size reduction with air separation and thermal purification in vacuo.

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* [In Russian: "total electrical energy", but this would be in contradiction with the statement in the last paragraph of the section (80% current efficiency).]

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The air separation method. Because of the great difference between the densities of tantalum (16.6 g/cm^3) and the components of the electrolyte, the latter are readily separated when the cathodic product is milled in a ball mill operating in a closed cycle with an air separator. This method permits the separation of tantalum from the bulk of the salts, which may be reused as the electrolyte.

The tantalum powder is then treated with water on beneficiation tables, which results in the removal of the electrolyte residues, and is then treated in porcelain vats with a hot mixture of hydrochloric and nitric acids in order to remove the impurities. The powder is then rinsed with water and dried.

Purification by thermal processing in vacuo. This method was developed in the USSR. The bulk of the salts is separated from the tantalum by fusion (melting) in an atmosphere of argon, and the residual salts are separated by vacuum evaporation. The apparatus used is shown in Figure 73 /14/.

The fusion and the vacuum evaporation are carried out in a thick-walled retort 1 made of refractory steel or nichrome. The crucible 7 with the cathodic deposit is placed in the upper part of the retort; the stopper closing the opening in the bottom of the crucible is replaced by a flange with a screen. A water-cooled condenser 3 is connected through flanges to the lower part of the retort; container 4, which is used to collect the molten electrolyte, is connected to the condenser. The electric furnace 2 is lowered over the retort. The retort is connected to a system of vacuum pumps producing a vacuum of 10^{-3} to 10^{-4} mm Hg, and with an argon cylinder.

The retort is evacuated, filled with argon, and heated to 1000° when the electrolyte melts. Vacuum is then created in the retort and the residual salt is removed by evaporation. The imperfectly sintered tantalum dendrites remain on the walls of the crucible; they are removed and easily powdered by milling. The molten electrolyte is returned to electrolysis.

The particle size of electrolytic tantalum powder is much larger than that of the powder prepared by thermal reduction with sodium. The average particle size of the cathodic product after milling and air separation is 30 to 70 μ, while after thermal processing in vacuum it is 100 to 120 μ.

The powders have the following approximate impurity contents: 0.1 to 0.2% O_2, 0.03 to 0.2% C, 0.03 to 0.1% Fe+Ni, 0.01% F, and up to 0.1% Si. The oxygen content is about one-tenth that of the powder produced by thermal reduction with sodium in vacuum, due to the larger particle size of the electrolytic powder and the correspondingly smaller amount of oxide film. Powders with a high carbon content (above 0.5%) may be treated with a mixture of concentrated sulfuric and nitric acids to oxidize the graphite particles.

The most important advantage of the electrolytic process is the production of better quality powders. The coarse electrolytic powders have a lower oxygen content which simplifies their conversion into bars by pressing and sintering.

Moreover, the specific consumption of electrical energy in the electrolytic process is lower than in the thermal reduction with sodium; if it is taken into account that the sodium is also produced by electrolysis.

The production of tantalum and niobium by electrolysis of their chlorides is of great interest. Tantalum and niobium pentachlorides dissolve in molten alkali chlorides yielding the complex salts $MeNbCl_6$ and $MeTaCl_6$

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(where *Me* — Na or K). Coarsely crystalline deposits of niobium and tantalum are formed on the cathode in the electrolytic decomposition of these complexes, while chlorine is evolved at the graphite anode.

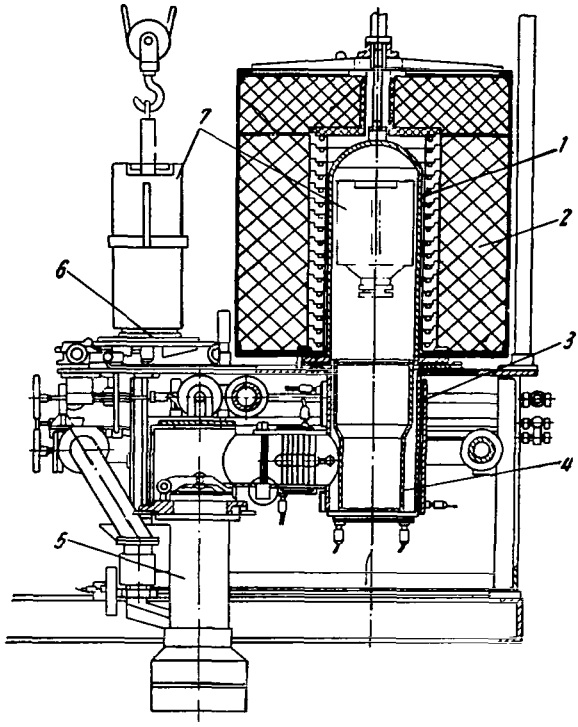

FIGURE 73. Installation for the vacuum-thermal processing of cathodic deposits.

1—retort; 2—electric furnace; 3—condenser; 4—container used to collect the electrolyte; 5—diffusion pump; 6—trolley for inserting the crucible cathode; 7—crucible cathode.

34. PRODUCTION OF NIOBIUM BY THE CARBIDE REDUCTION METHOD /13/

The carbide reduction method is based on the interaction between niobium pentoxide and niobium carbide in vacuo at 1800 to 1900°:

$$Nb_2O_5 + 5NbC \rightarrow 7Nb + 5CO.$$

Niobium carbide is made by heating a mixture of Nb_2O_5 with pure lamp black:

$$Nb_2O_5 + 7C \rightarrow 2NbC + 5CO.$$

The pentoxide-lamp black mixture is pelletized and the pellets are heated to 1800 to 1900° in a tubular graphite furnace, in a hydrogen or argon atmosphere, or to 1600° in a vacuum furnace. The less expensive method

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is to produce the niobium carbide in the tubular graphite furnace, with continuous motion of the pellets over the length of the furnace.

The pulverized niobium carbide is mixed (in a ball mill) with a small (3 to 5%) excess of niobium pentoxide. This provides for a more complete removal of the carbon (as CO) in the subsequent vacuum sintering of the compacts pressed from the powder.

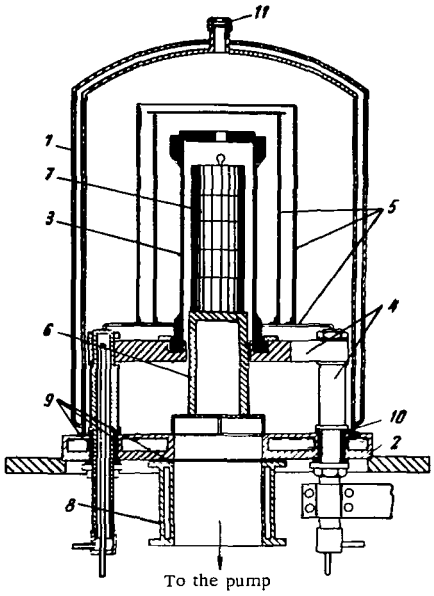

FIGURE 74. Diagram of a vacuum furnace with a graphite heating element.

1—water-cooled cover; 2—water-cooled base plate; 3—tubular graphite heating element; 4—current terminals; 5—screens; 6—support; 7—pelletized charge; 8—sleeve connector to the pump; 9—rubber seals; 10—washer (electrical insulator); 11—window.

The pentoxide-carbide mixture is pressed into bars under a pressure of 1 to 1.5 tons/cm^2. The bars are heated in vacuum furnaces with graphite heating elements (resistors) (Figure 74) or in vacuum induction furnaces with a graphite tube.

The reduction is carried out at 1800 to 1900°, at $\sim$ 0.01 to 0.001 mm Hg.

The reduction takes place through intermediate stages involving the formation of lower oxides (NbO_2 and NbO) and a carbide, Nb_2C.

Since the oxides NbO_2 and NbO are fairly volatile at 1800 to 1900° in vacuo, the gaseous oxides react with niobium carbide, a fact which explains the high rate of the reduction.

The bulk of carbon monoxide is evolved rapidly, and a large proportion is evacuated by the pump within a few minutes. The process is completed when the vacuum attains $10^{-2} - 10^{-3}$ mm Hg.

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The product consists of sintered porous niobium pellets, which retain the initial shape of the compacts but with a certain reduction in size.

The pellets are forwarded to electron-beam melting. They may also be sintered in vacuo at 2300 to 2350°, yielding a ductile metal. In another technological process, the pellets are pulverized and the powder is pressed into bars and sintered in vacuo. To facilitate the comminution the pellets are hydrogenated (heated in hydrogen at 360°). The metal absorbs hydrogen and becomes brittle.

The carbide reduction method has the advantage of a high direct yield of the useful metal (at least 96%) and the use of a cheap reducing agent. The method may also be used for the production of tantalum and tantalum-niobium alloys. It has the disadvantage of requiring the use of high-temperature vacuum furnaces of complex design.

35. PRODUCTION OF TANTALUM AND NIOBIUM BY REDUCTION OF THEIR CHLORIDES

The production of tantalum and niobium from their chlorides has recently attracted attention; this method is especially suitable when the processing of concentrates results in chlorides as the end product.

Niobium and tantalum pentachlorides may be reduced by metals (sodium, magnesium) or hydrogen. These methods are not industrially used as yet, and they will be described only briefly on the basis of laboratory data /1/.

Reduction of chlorides by magnesium is an exothermic reaction:

$$2TaCl_5 + 5Mg \rightarrow 2Ta + 5MgCl_5 + 38 \text{ kcal}.$$

The heat of reaction is sufficient for a self-sustained reaction. The reduction is carried out in a steel crucible containing a charge consisting of $TaCl_5$, magnesium turnings and potassium and sodium chlorides which act as flux (reducing the reaction rate by decreasing the specific heat effect of the process). The crucible is slowly lowered into a furnace heated to about 750°. The reaction is rapid. The tantalum particles formed are protected against oxidation by the molten salt mixture consisting of $MgCl_2$, NaCl and KCl.

The powder is freed from chlorides by washing with water and dilute hydrochloric acid, and is then rinsed with alcohol and dried in vacuum. The yield of tantalum powder is high (about 98%). The particle size of the powder is between 1 and 10 μ. The powder contains 0.1—0.5% Mg, ~ 0.3% Fe, and ~0.1% Ti.

The same method may be used to produce niobium or niobium-tantalum alloys, by simultaneous reduction of their chlorides.

In order to produce tantalum and niobium powders of higher purity, it is preferable to reduce the gaseous chlorides by liquid magnesium, as in the production of zirconium.

Reduction of tantalum and niobium chlorides to the metal by hydrogen is carried out at temperatures above 600°. The production of niobium has been studied more thoroughly, and the process may be effected with simultaneous removal of iron chloride from niobium chloride and the separation of tantalum and niobium. According to one method which has been described, niobium pentachloride is produced by chlorination of ferroniobium, containing 70% Nb + Ta, 24.7%Fe, 1.7% Mn, 1.5% Al, 1% Ti, 0.3% W, 0.2% Sn, and 0.2% Cr. A mixture of $NbCl_5$, $TaCl_5$, and $FeCl_3$ was condensed after chlorination at about 1000°. In order to separate the iron, the chlorides were distilled in hydrogen at 350°. Under these conditions ferric chloride was reduced to the nonvolatile $FeCl_2$. The tungsten present as an impurity was separated at the same time.

Tantalum was separated from niobium by passing a mixture of the gaseous chlorides and hydrogen through a tube heated to 500—550°. Under these conditions niobium pentachloride was reduced to the nonvolatile $NbCl_3$, while $TaCl_5$ was not reduced and was collected by condensation at low temperatures.

Niobium trichloride is stable in air. It is reduced to the metal by hydrogen at 800—1000°; the reduction is carried out in molybdenum boats placed in a tubular quartz furnace. The powder produced by the above method is characterized by low oxygen and nitrogen contents (~ 0.03 and ~ 0.05% respectively). The disadvantage of the process is the low reduction rate and the difficulties caused by the side reaction — the disproportionation of $NbCl_3$ with the formation of niobium and the volatile higher chlorides ($NbCl_4$ and $NbCl_5$).

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36. PRODUCTION OF SOLID, DUCTILE TANTALUM AND NIOBIUM

Solid tantalum and niobium were previously produced solely by powder metallurgy techniques. Melting techniques, which permit the production of large ingots, have been recently developed. Both metals can be melted in arc furnaces with cooled copper crucibles, or in electron-beam furnaces. In contrast to tungsten and molybdenum, both the sintering and melting of pressed tantalum and niobium bars are carried out in high vacuum. As a result, the metals are freed from adsorbed gases, and from oxygen, carbon, silicon and many other elements present as impurities.

The powder metallurgy method

The fundamentals of the method have been discussed in the chapter "Tungsten". The process comprises two stages: pressing of the powder into bars and sintering.

Pressing. Tantalum and niobium powders are pressed into bars with rectangular (when intended for rolling into sheets) or square (when intended for wire drawing) cross sections. The length of the bars is from 600 to 750 mm, their cross section — from 4 to 20 cm^2.

The pressing conditions depend on the nature of the starting powder. The fine tantalum and niobium powders produced by thermal reduction with sodium have a large specific surface and are thus pressed at lower pressures than the electrolytic powders. The pressure needed for tantalum powder is 3 to 5 tons/cm^2, and for niobium powder about 1 ton/cm^2.

Electrolytic powders have a coarser particle size, and are pressed under 7 to 8 tons/cm^2.

The porosity of the pressed bars is 25 to 30% by volume for powders produced by thermal reduction with sodium, and about 20% by volume for electrolytic powders. Hydraulic presses similar to those used in the pressing of tungsten powder are used.

Sintering. A number of complex physical and chemical processes occur when tantalum and niobium bars are heated in vacuo; each process takes place within a certain temperature range following the increase in temperature. The occurrence of these processes is evidenced by the changes in certain properties of the bars: electrical resistivity, density, weight, microstructure, and by the impurity content of the metal. The changes in electrical resistivity are especially indicative since the resistivity is strongly affected by the presence of impurities and the porosity of the bar.

Figure 75 gives curves showing variations in the specific electrical resistivity, density and weight of a tantalum bar (per cm^2 of its surface) as a function of the sintering temperature.

The sharp decrease in electrical resistivity occurring when the bar is heated in vacuum to 600 to 650° is due to the escape of the hydrogen from the metal. The electrical resistivity does not drop significantly between 600 and 1100°. Above 1100° there is a decrease in the electrical

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resistivity up to 1600°. The resistivity increases somewhat between 1600 and 1900° and drops to a minimum as the temperature is further increased.

The decrease in resistivity at 1100 to 1600° is associated with incipient sintering and further removal (evaporation) of certain impurities (alkali metals — sodium and potassium, and their salts), as well as with incipient elimination of carbon as carbon monoxide, formed by the interaction of carbon with the oxide film.

A slight increase in the electrical resistivity between 1600 and 1900°, which is accompanied by an increase in the weight of the bar, is probably caused by some slight absorption of gases (nitrogen, oxygen) which are present in the interior of the vacuum vessel used for the sintering.

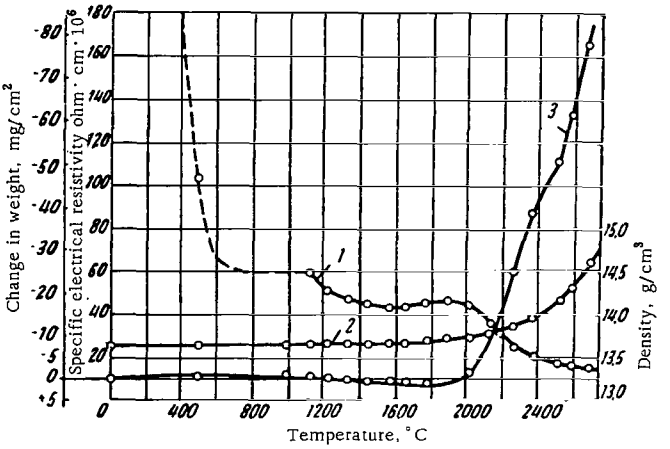

FIGURE 75. Changes in the properties of pressed tantalum bars during sintering in vacuum.

1—electrical resistivity; 2—density; 3—changes in weight.

A decrease in the electrical resistivity and a considerable decrease in weight take place above 1900°. Intensive elimination of carbon and silicon (as CO and the lower oxide SiO), sublimation of lower tantalum oxides (e. g., TaO_2) as well as vaporization of impurities (titanium, iron, nickel) take place at 1900 to 2300°. The removal of impurities is accompanied by a simultaneous increase in the density (contraction) of the bars. Vaporization of a part of the tantalum and a further contraction of the bars is observed at 2400 to 2600°.

The same processes take place during the sintering of niobium bars, but the temperature ranges are somewhat lower.

It will be seen that the sintering in vacuo is accompanied by the removal of a number of impurities from the bars. The oxygen is removed as CO, SiO, and lower tantalum or niobium oxides. A considerable proportion (up to 5 to 10% by weight) of the metal may be lost as the lower niobium or tantalum oxides. Thus, it is expedient to remove most of the oxygen as CO. Hence, a calculated amount of carbon (as pure carbon black) is added to the starting powder if it contains a large amount of oxide films.

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When the powders contain a large amount of carbon and a small amount of oxide film, it is advisable to add tantalum (or niobium) oxide to the starting powder in order to remove the carbon during the sintering of the bars.

Because of the considerable amount of gases evolved during the sintering, the temperature must not be raised too quickly as the rapid sintering and contraction of the bar causes the open pores to close up and thus interferes with the removal of the volatile impurities. This may result in high pressures being produced within the closed pores and in swelling and formation of large pores and cavities in the bars.

The sintering conditions depend on the composition and particle size of the powders. However, in all cases the temperature must be raised stepwise and the bar must be held for some time at a constant temperature at each successive stage.

As an illustrative example, one set of conditions recommended for the sintering of bars pressed from electrolytic tantalum powder is shown in Table 26.

TABLE 26

Sintering parameters of tantalum bars (20×20×600 mm) pressed from electrolytic powder

Temperature range, °C	Mode of raising of the temperature and holding times	Total time (raising and holding)
Up to 1750	After each 100° hold for 4 minutes	1 hour 10 minutes
1750—2000	After each 20° hold for 4 minutes	50 minutes
2000	Hold for 60 minutes	1 hour
2000—2600	After each 25° hold for 4 minutes	1 hour 40 minutes
	Total sintering time	4 hours 40 minutes

The total sintering time depends on the amount of impurities in the starting powder. The sintering time for bars of tantalum powders made by thermal reduction with sodium is 8 to 12 hours, that of electrolytic powder bars is 4 to 6 hours.

The only difference between the sintering of bars made of tantalum and niobium powders is that in the case of niobium the maximum sintering temperature is 2200 to 2300°.

In order to achieve satisfactory sintering and removal of impurities, it is necessary not only to maintain the required temperature conditions, but also to provide for a rapid evacuation of the gases. The residual pressure in the sintering furnace must be about 10^{-4} to 10^{-5} mm Hg.

The residual porosity of the sintered bars is usually 10 to 15%.

A virtually pore-free metal is produced by forging of the sintered bar followed by vacuum annealing at a high temperature. Twice-repeated forging and annealing produces pore-free bars which are used for sheet rolling or wire drawing.

In most cases tantalum and niobium bars are heated directly by passing through an electric current (Figure 76) as is done in the case of tungsten

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bars*; the only difference being that the space under the cover, which contains the bar, is connected to a vacuum pump. In addition, graphite and molybdenum sheet screens are placed around the bar in order to reduce heat losses and to provide a more uniform heating of the bar.

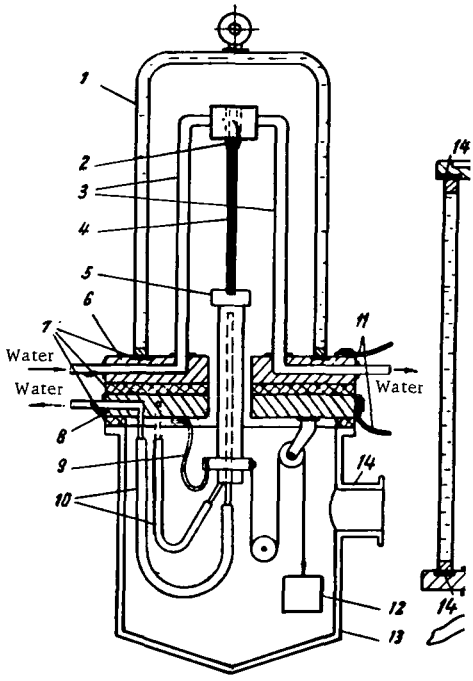

FIGURE 76. Diagram of a vacuum apparatus for high-temperature sintering of tantalum and niobium bars.

1 —cooled steel cover; 2—upper stationary contact; 3—copper supports feeding the current to the upper contact; 4—bar to be sintered; 5—lower movable contact; 6—steel plate; 7—rubber rings; 8—steel plate; 9—flexible bus bar serving as current terminal; 10—rubber hose for the feed and discharge of water to the lower contact; 11—bus bars; 12—weight; 13—lower cover; 14—connection to the vacuum pump.

Large pressed bars and products having a complex shape are heated indirectly in induction or resistance-heated furnaces.

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* The electrical conductivity of bars pressed from tantalum powders made by thermal reduction with sodium is often too low to permit direct heating by the current. To increase the conductivity, the bars are presintered at 1000—1200° in a horizontal tubular vacuum furnace with an alundum tube heated by a molybdenum wire coil. Bars pressed from niobium powder and bars pressed from electrolytic tantalum powder usually do not require presintering.

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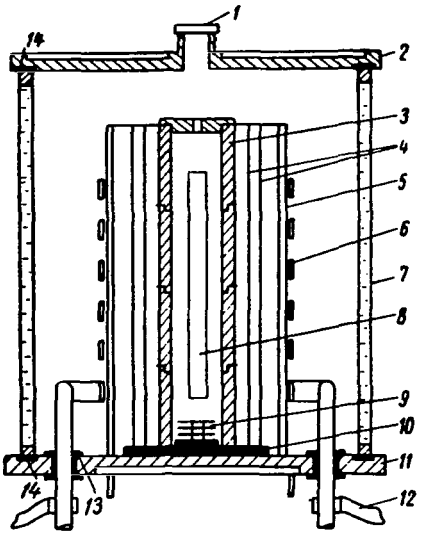

FIGURE 77. Diagram of induction vacuum furnace.

1 — window; 2 — water-cooled lid; 3 — tungsten cylinder heated by induction current; 4 — molybdenum screens; 5 — quartz tube; 6 — inductor (water-cooled copper tube); 7 — water-cooled cylinder; 8 — bar to be sintered; 9 — molybdenum screens; 10 — graphite support; 11 — water-cooled plate; 12 — bus bars (current leads to the inductor); 13 — vacuum seals and electrical insulation; 14 — rubber rings.

A diagram of a vacuum induction furnace used for sintering is shown in Figure 77. The bar to be sintered is suspended in a tungsten tube (made of tungsten rings) heated by an inductor mounted on a quartz tube. The heat is transferred by radiation from the tungsten tube to the bar. To reduce heat losses the tungsten tube is surrounded by cylindrical molybdenum screens which are cut so that the formation of closed-circuit induction currents is eliminated. It is recommended that the inductor be fed with a frequency of 2 to 4 kilocycles/sec /1/.

The melting of niobium and tantalum /17/

The arc-melting method. Niobium and tantalum may be melted in arc furnaces with a consumable electrode and a cooled copper crucible; the construction of these furnaces has been described in the chapter "Molybdenum". Sintered bars are used as consumable electrodes. They are melted in order to produce larger bars which are used for sheet rolling.

Since in the arc-melting process the metal remains in the molten state only for a short time, purification by vaporization of impurities is

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insufficient. This is especially true in the case of niobium, whose melting point is about 500° lower than that of tantalum. Because of the higher melting point of tantalum, arc melting of this metal results in a more complete removal of impurities.

Electron-beam melting. This process, which was developed only recently, permits very high-purity niobium and tantalum ingots to be produced.

Electron-beam heating of metals is based on the conversion of most of the kinetic energy of the electrons into heat upon impact against the metal surface. A smaller proportion of the kinetic energy is converted into X-ray energy.

The impact of an electron moving with a velocity v, with the body to be heated results in an energy distribution obeying the equation:

$$\frac{mv^2}{2} = Q + \frac{hC}{\lambda},$$

where m is the mass of the electron;

Q is the fraction of kinetic energy converted into heat;

hC/λ is the fraction of kinetic energy converted into X-ray energy. Here h is the Planck constant, C is the velocity of light and λ is the wavelength of the X-rays.

An increase in the velocity of the electrons is accompanied by an increase in the proportion of the energy emitted as X-rays since the X-rays become harder (i. e., their wavelength becomes shorter). Thus, protective measures against radiation must be taken.

The electron velocities in electron-beam melting equipment are therefore limited to acceleration voltages not exceeding 30 to 35 kV. The equipment consists of the following parts:

1) an electron gun, in which a directed electron beam is produced;
2) a melting chamber;
3) a high-vacuum system;
4) a source of high-voltage direct current.

The maintenance of a high vacuum in the system is required in order to reduce to a minimum the losses of energy caused by the impact of the electron beam on the gas atoms and molecules in its path to the body to be heated, and to extract impurities from the molten metal which are volatilized during the melting.

A simplified diagram of electron-beam melting is shown in Figure 78. The electron gun (which creates a focused, intense electron beam) consists of a cathode, an anode, a control grid, and focusing and deflecting coils. An incandescent tungsten coil may be used as the cathode, but indirectly heated cathodes made of pure tungsten and tantalum are more frequently used. A high negative potential is applied to the cathode. The electron beam passes through a grounded hollow anode. A cylindrical control electrode (known as a modulator or a grid) with a negative potential is placed between the cathode and the anode. The shape of the electron beam and the density of the space charge (around the cathode) are controlled by varying the potential of the control grid. The focusing and the deflection of the electron beam are accomplished by means of magnetic and an electrostatic field

The design of a furnace used for electron-beam melting is shown in Figure 79. The furnace has a single electron gun, with an independent

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evacuation system. The electron beam penetrates into the working chamber of the furnace through a special diaphragm which produces considerable resistance to gas flow and thus ensures that the vacuum in the gun space is higher than that in the melting chamber. The electron beam is directed onto the end of the metal to be melted (a pressed, sintered bar). The electron beam also impinges on a water-cooled crystallizer, in which the metal resides for a certain time in the molten state.

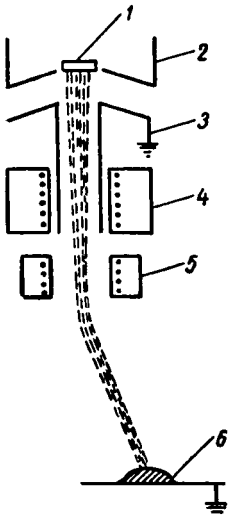

FIGURE 78. Diagram of electron-beam melting.

1—cathode (under high voltage); 2—control grid; 3—anodic tube; 4—focusing coil; 5—deflecting coil; 6—metal to be melted.

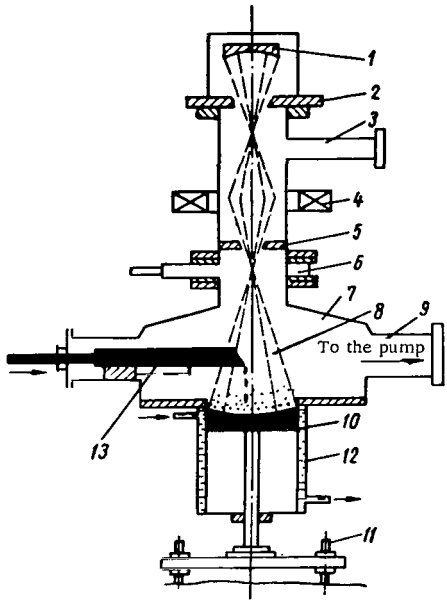

FIGURE 79. Diagram of an electron-beam melting furnace.

1—electron gun cathode; 2—electron gun anode; 3—sleeve connection to the vacuum system; 4—electromagnetic coil (lens); 5—diaphragm separating the melting chamber of the furnace from the electron gun; 6—gate; 7—melting chamber; 8—electron beam; 9—sleeve connection to the vacuum system; 10—melted ingot; 11—ingot drawing mechanism; 12—water-cooled copper crystallizer; 13—sintered bar, to be melted.

The melting is carried out in high vacuum (10^{-4} to 10^{-6} mm Hg) which ensures the removal of impurities which are vaporized at the melting temperature. Thus, the melting of niobium is accompanied by the removal of oxygen (as CO and lower oxides), nitrogen, hydrogen, iron, nickel, chromium, and aluminum. However, refractory metals such as molybdenum, tungsten, and tantalum are not removed.

The approximate power of electron-beam equipment used for the melting of niobium and tantalum ingots of various diameters /27/ is given below:

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Niobium:					
	ingot diameter, mm	50	75	100	
	power, kw	30	60	120	
Tantalum:					
	ingot diameter, mm	35	50	75	100
	power, kw	30	60	120	240

Up to 130 kg niobium may be melted at 120 kw per hour.

The furnace just described is charged with sintered bars. However, powder, sponge or turnings may also be melted in the crucible.

Electron-beam melting has the advantages of producing a high-purity metal (because the molten metal may be held in high vacuum for a prolonged time), of low cost (the efficiency of the system is more than 95%), and of the fact that the metal to be melted may be in any form (bars, powder, turnings, waste lumps) while the use of arc melting involves the preparation of consumable electrodes.

Vacuum pumps and vacuum systems

The vacuum of the order of 10^{-4} to 10^{-6} mm Hg or higher, which is required for the melting, is usually created by two types of pumps operating in conjunction — a mechanical oil pump (preliminary vacuum pump) and a diffusion pump. The mechanical pumps create a vacuum of 0.05 to 0.5 mm Hg, which is required for the operation of the diffusion pump that creates a higher vacuum and ejects the evaucated gas into the mechanical pump.

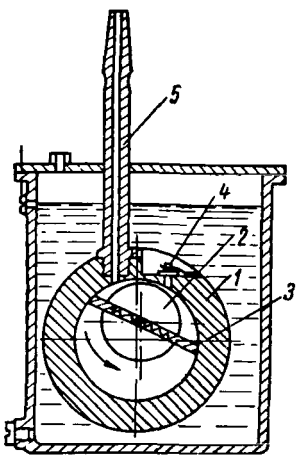

FIGURE 80. Diagram of a mechanical (rotary) oil pump.

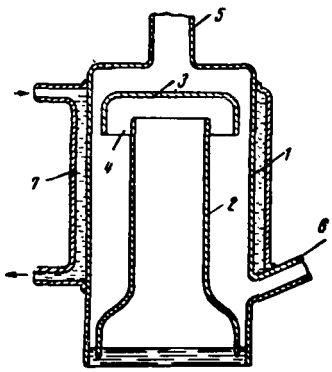

FIGURE 81. Diagram of a diffusion pump.

Mechanical pump. A diagram of one of the most commonly used mechanical pumps — the rotary oil pump — is shown in Figure 80. The

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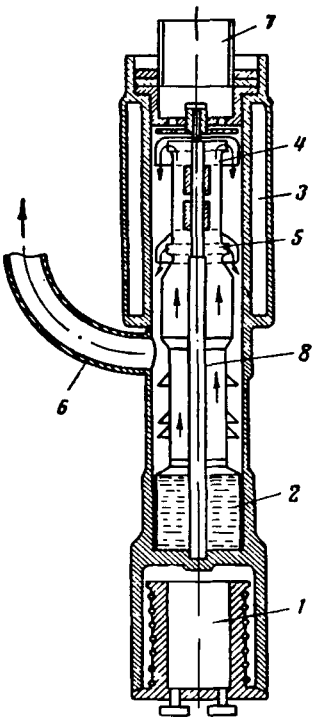

FIGURE 82. Two-stage oil diffusion pump.
1—heater; 2—boiler; 3—cooler; 4—and 5—ring-shaped nozzles; 6—connection to preliminary vacuum pump; 7—connection to the system to be evacuated; 8—copper rod (serving as heat-transfer medium).

pump consists of a steel cylinder 1 with an excentric rotor 2 inside it. The rotor carries blades 3 set within grooves; the blades press (with the aid of springs) against the inner surface of the cylinder. When the rotor is set in motion, the blades act as pistons. When the rotor is rotated in a counterclockwise direction, the air is pumped through sleeve connection 5 and expelled through the escape valve 4 into the space above the oil. The cylinder is immersed in oil which serves as a lubricant and provides a hermetic seal on the pump.

One- and two-stage pumps of this type are manufactured. The two-stage pump consists of two pumps connected in series and mounted on a common shaft.

Diffusion pumps. Diffusion pumps operating on mercury or oil vapor, but based on the same principle, are used in industry. A diagram of a diffusion pump is shown in Figure 81. The pump consists of a water-cooled cylindrical steel vessel 1 containing mercury or oil (which have a low vapor pressure at ambient temperatures) on the bottom. A funnel-shaped tube 2 with a cap 3 suspended over it (thus creating a ring-shaped nozzle 4 in the upper part of the cylinder) is mounted inside the vessel. The bottom of the pump is heated. The mercury or the oil evaporates, the vapors rise within the tube, strike the cap and are thrown at a high velocity from the nozzle onto the cooled walls of the body. The gas from the sleeve connection 5 is entrained downwards with the vapor stream and is pumped out through the sleeve connection 6 by the mechanical pump (described above). The body walls of the pump are cooled by the water jacket 7.

Two- and three-stage diffusion pumps with a number of nozzles mounted over each other (Figure 82) are produced commercially. Oil-diffusion pumps are being increasingly used. Purified oils (n-dibutyl phthalate, butylbenzene phthalate) which have a very low vapor pressure at 20° are used for the purpose. To prevent the penetration of oil vapor into the furnace, the vacuum system is fitted with "freezing" traps (cooled by liquid air or nitrogen).

A typical high-vacuum system is shown in Figure 83. The evacuation is effected at first with the mechanical pump, the diffusion pump being disconnected. The diffusion pump is connected when the vacuum in the system becomes as low as 0.05 to 0.5 mm Hg; it expels the evacuated gas into the preliminary-vacuum cylinder. In each case the vacuum system is computed and the pumps selected from the furnace size, the amount of gases to be evaucated, and the rate of evaucation required.

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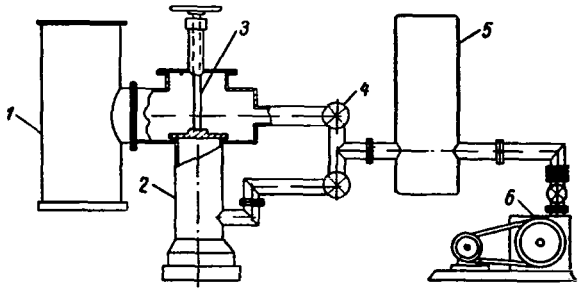

FIGURE 83. A typical high-vacuum system.

1—volume to be evacuated; 2—diffusion pump; 3—vacuum valve; 4—vacuum faucets; 5—preliminary vacuum cylinder; 6—mechanical (rotary) pump.

The high-vacuum oil-diffusion pumps made in the USSR have an evacuation rate of 100 to 8000 1/sec or more in the pressure range $2 \cdot (10^{-4} - 10^{-5})$ mm Hg.

37. RECOVERY OF METALLIC TANTALUM AND NIOBIUM WASTES

Two types of wastes accumulate in the production of the solid metals.

Bar fragments. These consist mainly of the trimmed bar ends after high-temperature sintering since the bar ends clamped in the contacts do not reach the maximum sintering temperature. Fragments of discarded bars (sintering wastes) also belong to this type of wastes. However, in a well-designed production such waste may be altogether eliminated.

Wastes from mechanical processing (cutting, rolling wastes). This type of waste also comprises processed tantalum and niobium-anodes, grids, and other parts from discarded radio valves and rectifiers.

The two types of wastes mentioned above consist of the pure metals. They are recovered (reconverted into useful metal), thus increasing the degree of extraction of the metal and reducing its price. Tantalum and niobium wastes are pulverized and the powders are sent to the bar-pressing stage.

Since tantalum and niobium are ductile, their crushing is difficult. In the production of powders, use is made of the embrittlement of tantalum and niobium resulting from the absorption of hydrogen. Tantalum and niobium wastes are heated in hydrogen (niobium to 360° and tantalum to 500°). The hydrides produced are readily crushed to a fine powder in a steel ball mill. The powder is treated with hydrochloric acid to free it from iron (acquired contamination by friction during milling). The powder is then rinsed with water, dried, and combined with the powder sent to pressing. The hydrogen is removed from the metal during low- and high-temperature vacuum sintering.

Wastes may also be reprocessed by melting in arc or electron-beam furnaces.

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Chapter IV

TITANIUM

38. GENERAL DATA ON TITANIUM

Brief historical note

The element titanium was discovered in 1791 by Gregor (a British amateur mineralogist) in the black magnetic (iron-bearing) sands of Menaccan in Cornwall. The new element was called menaccanite.

In 1795 the German chemist Klaproth investigated the mineral rutile and found that it was the oxide of a new element which he called titanium. It was subsequently established that titanium is identical with menaccanite.

Prior to 1849 it was believed that the metal-like titanium carbonitride found in the slags of blast furnaces was metallic titanium. Relatively pure titanium was obtained by Hunter in 1910 — 120 years after its discovery.

The industrial utilization of titanium both as chemical compounds and as an alloy additive dates from the first decades of the twentieth century.

Titanium attracted interest as a potential structural material during the Second World War. This resulted in the development of industrial methods for the production of the ductile metal and to the introduction of large-scale production of the metal and its alloys in a number of countries.

Properties of titanium

Titanium has the appearance of steel. The pure metal is ductile and is easily worked by pressure. Two crystalline modifications of titanium are known. The form which is stable up to 882° is α-titanium which has a hexagonal close-packed lattice with the parameters $a = 2.951$ Å and $c = 4.692$ Å. Above 882° α-titanium is converted into β-titanium, with a body-centered cubic lattice. The lattice parameter of β-titanium is $a = 3.3065$ Å (at 900°). Some physical properties of titanium are reported below, while the mechanical properties of titanium are listed in Table 27.

Atomic number	22
Atomic weight	47.90
Density, g/cm^3	4.51 (α-titanium)
Melting point, °C	1668 ± 4
Boiling point, °C	~ 3300
Superconductance transition temperature, °K	0.53

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Vapor pressure, mm Hg, at temperatures, °C	
1227	10^{-6}
1442	10^{-4}
1727	1
2477	10
Heat of fusion, cal/g	~104
Specific heat (in the range 0 to 100°) cal/g, °C	0.127
Thermal conductivity (in the range 0 to 200°) cal/cm·sec, °C	0.04
Linear expansion coefficient at 20 to 300°C	$8.2 \cdot 10^{-6}$
Specific electrical resistance, ohm·cm·10^6 at:	
20°C	42
800°C	180
Electron work function, eV	4.09
Thermal neutron capture cross section, barns	5

TABLE 27

The mechanical properties of titanium

Method of production and processing	Tensile strength kg/mm²	Yield point (at a residual elongation of 0.2%) kg/mm²	Elongation, %	Young's modulus, kg/mm²	Hardness kg/mm²
High-purity titanium (iodide method) after vacuum annealing at 800°C	27—34	14—16.9	40—55	9850—10900	73
The same, after deformation (50% reduction)	68—75	61—63	5—11	11300	—
Prepared by reduction of titanium chloride with magnesium and melted in an arc furnace with a cooled copper crucible, after annealing	53—60	51—55	20—25	11200—11600	120—185
The same, after deformation (50% reduction)	75—83	73	12—14	—	250—280

The mechanical properties are strongly affected by the purity of the metal and its mechanical and thermal processing history.

Titanium is characterized by its ability to absorb gases — oxygen, nitrogen, and hydrogen. These gases are soluble in titanium up to a certain limit. The presence of even a small amount of oxygen and nitrogen reduces the ductility of titanium (see Figure 84). Very small amounts of hydrogen (0.01 to 0.005%) noticeably increase the brittleness of titanium, which is measured by means of the impact strength (Figure 85).

Titanium is resistant to the effect of air at ambient temperatures. When heated to 400 to 550° the metal is coated with an oxide-nitride film which adheres strongly to the metal and prevents further oxidation. At higher temperatures there is an increase in the rate of oxidation and in the solubility of oxygen in titanium.

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Titanium reacts with nitrogen at temperatures above 600° with the formation of nitride (TiN) films and solid solutions of nitrogen in titanium. Titanium nitride is very hard and melts at 2950°. Titanium absorbs hydrogen with the formation of solid solutions and hydrides (TiH and TiH_2). The solubility of hydrogen in α-titanium is about 1% by weight (or 33% (atomic)). Unlike oxygen and nitrogen, the absorbed hydrogen may be expelled almost quantitatively from titanium by heating in a vacuum at 1000 to 1200°.

Titanium reacts with carbon and carbon-containing gases (CO, CH_4) at high temperatures (above 1000°), yielding a hard, refractory carbide (TiC, mp 3140°). The presence of carbon (as an impurity) has a strong effect on the mechanical properties of titanium (see Figure 84).

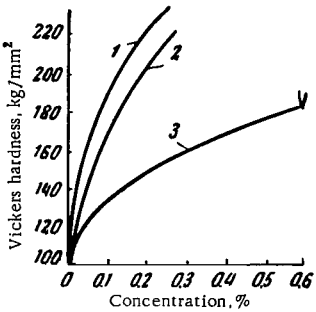

FIGURE 84. Effect of nitrogen, oxygen, and carbon on the hardness of titanium after melting.

1 — metal containing nitrogen; 2 — metal containing oxygen; 3 — metal containing carbon.

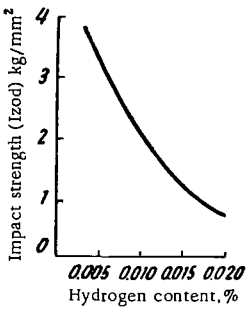

FIGURE 85. Effect of hydrogen on the impact strength of titanium.

Titanium reacts with fluorine, chlorine, bromine, and iodine at relatively low temperatures (100 to 200°), yielding the volatile titanium halides.

From the standpoint of its corrosion resistance titanium resembles the chromium-nickel stainless steels. The metal is not corroded by cold or boiling water. Titanium is virtually unaffected by cold or hot nitric acid of any concentration, due to the formation of an adherent, protective oxide film. Titanium resists the effect of dilute (up to 5%) sulfuric acid at room temperature. However, the rate of corrosion increases as the acid concentration is increased, reaching a maximum at 40% H_2SO_4, then dropping to a minimum at 60% H_2SO_4, increasing to a second maximum at 80% H_2SO_4, and decreasing again at higher acid concentrations (Figure 86).

Titanium displays a satisfactory resistance to dilute (5 to 10%) hydrochloric acid at room temperature. However, the rate of corrosion increases rapidly when the acid concentration or the temperature is increased. The corrosion of titanium in hydrochloric acid may be considerably reduced by the addition of small amounts of an oxidizing substance (HNO_3, $KMnO_4$, K_2CrO_4, and copper or iron salts) to the solution.

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Titanium dissolves readily in hydrofluoric acid. Titanium is resistant to cold and hot solutions of alkali hydroxides (at concentrations of up to 20%).

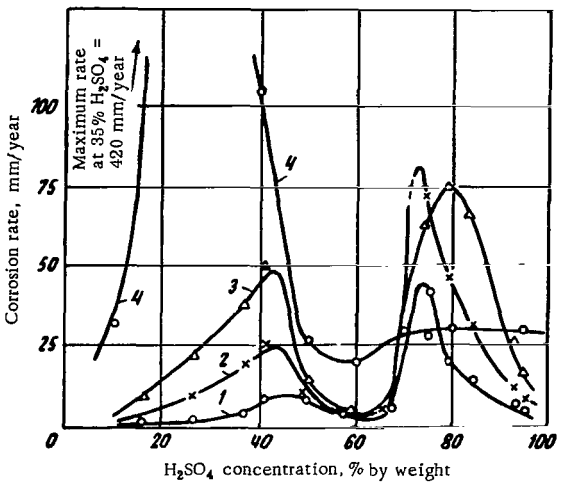

FIGURE 86. Effect of the acid concentration on the corrosion rate of titanium in H_2SO_4.

1—at 30°C; 2—at 40°C; 3—at 50°C; 4—at 100°C.

The high resistance of titanium to corrosion in sea water and in solutions of chlorides of a number of metals are of great importance.

The properties of titanium compounds

Titanium belongs to Group IV of the periodic system. In its most stable and important compounds titanium is tetravalent. There are also compounds of di- and trivalent titainium. The lower valency compounds are unstable in aqueous solutions, in which they act as strong reducing agents.

TABLE 28

Properties of titanium oxides

Oxide	Melting point, °C	Density	Heat of formation, kcal/mole	Crystalline structure and lattice parameters
TiO_2	~1850	4.18—4.25	225.5	Tetragonal (rutile type), a=4.48 Å, c=2.95 Å
Ti_2O_3	1900—2130	4.6	362.9	Trigonal (corundum type), a = 5.14 Å, c = 13.61 Å
TiO	1750—2020	4.93	123.9	Face-centered cubic. The composition fluctuates between $TiO_{0.69}$ and $TiO_{1.35}$. The lattice parameter fluctuates from a = 4.182 to a = 4.152 Å

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Oxides. Titanium forms three simple oxides in which it is tetra-, tri- and divalent: TiO_2, Ti_2O_3, and TiO. In addition, there are oxides of intermediate composition containing titanium atoms in various valency states. For instance, Ti_3O_5 (or $Ti_2O_3 \cdot TiO_2$) is one of these oxides. The higher oxides are amphoteric, but the lower oxides are basic. Some of their properties are listed in Table 28.

Titanium dioxide is one of the most important products obtained by processing of titanium-containing raw materials. The pure oxide is white. It occurs in nature in the form of three minerals — rutile, anatase, and brookite, which are allotropic modifications of titanium dioxide. Rutile is the most stable of these modifications. Titanium dioxide is virtually insoluble in water and dilute acids. It dissolves in hot concentrated sulfuric, hydrochloric, and nitric acids, as well as in hydrofluoric acid. In acid solutions titanium is present either as the Ti^{4+} cation or as a divalent cation — TiO^{2+} (titanyl ion). Titanic acid salts (titanates) are formed when titanium dioxide is fused with alkalies.

Titanium sesquioxide (Ti_2O_3) is a dark-violet powder. It may be produced by reduction of TiO_2 with hydrogen at 1100 to 1200° or with carbon at 1350 to 1400°. Ti_2O_3 is sparingly soluble in water. It dissolves in hot sulfuric acid, yielding violet-colored solutions of titanium sulfate (in which titanium is trivalent).

Titanium monoxide (TiO) is a golden-yellow substance with a metallic luster. Titanium monoxide is produced by heating a mixture of titanium dioxide and titanium powder in vacuo at 1550° or by reduction of TiO_2 with magnesium, aluminum or carbon. Titanium monoxide is insoluble in water. It reacts with sulfuric and hydrochloric acids with the evolution of hydrogen and the formation of trivalent titanium solutions.

Titanic acids. A gelatinous precipitate consisting of orthotitanic (or α-titanic) acid (H_4TiO_4) is formed in the cold when sulfuric or hydrochloric acid solutions are neutralized. The orthotitanic acid is converted into a more stable substance — metatitanic (or β-titanic) acid (H_2TiO_3) when the solution is boiled or allowed to stand for a prolonged time. In contrast to orthotitanic acid, metatitanic acid does not dissolve in cold dilute inorganic acids and alkali solutions. Metatitanic acid dissolves in hot, concentrated sulfuric acid (at concentrations of 60 to 70% and higher) and in hydrofluoric acid.

Titanium is characterized by the formation of pertitanic acids, which are produced by the effect of hydrogen peroxide on acid or neutral solutions of tetravalent titanium compounds.

Pertitanic acids having the compositions H_4TiO_5 and H_4TiO_8, as well as their salts, are known to exist. Solutions containing pertitanic compounds are yellow (at low concentrations) or orange-yellow (at high concentrations). This is used in the analytical determination of titanium.

Titanates. Titanic acid salts, titanates, are formed when titanium dioxide is fused with alkalies. There are meta- and orthotitanates (Na_2TiO_3, Na_4TiO_4), as well as polytitanates in which the molar ratio $TiO_2 : Na_2O > 1$, e.g., $Na_2Ti_2O_5$, $Na_2Ti_3O_7$. Alkali titanates are sparingly soluble in water.

Of the other metal titanates we may mention calcium titanate $CaTiO_3$ which is found in nature as the mineral perovskite; iron titanate $FeTiO_3$, found in nature as the mineral ilmenite; calcium silicotitanate $CaO \cdot TiO_2 \cdot SiO_2$, found in nature as the mineral sphene; and barium titanate $BaTiO_3$

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which has an extremely high dielectric constant and which is used for the production of high-capacity electrical condensers.

Titanium sulfates. Solutions containing mainly titanyl sulfate $TiOSO_4$ are formed when titanium dioxide or metatitanic acid are dissolved in sulfuric acid. The normal sulfate $Ti(SO_4)_2$ has not been isolated from aqueous solutions, although it is possible that in strongly acid solutions part of the titanium is present as Ti^{4+} ions. Titanyl sulfate, which crystallizes from solutions as the dihydrate $TiOSO_4 \cdot 2H_2O$, is the only stable sulfate known.

The stability of titanium sulfate solutions varies depending on the concentrations of the titanium and the sulfuric acid. When the solutions are diluted and heated, the sulfates hydrolyze with the precipitation of the sparingly soluble metatitanic acid:

$$TiOSO_4 + 2H_2O \rightarrow H_2TiO_3 + H_2SO_4.$$

This reaction is used in the manufacture of titanium dioxide.

The sulfates of tetravalent titanium are readily reduced in solution (for instance, by zinc or iron) to the trivalent titanium sulfate $Ti_2(SO_4)_3$ or the acid salt $Ti_3H(SO_4)_5$. Ti^{3+} ions are violet.

Halides. Titanium combines with halogens yielding volatile higher halides of the type TiR_4 (where R is F, Cl, Br, or I). In addition, there are halides in which titanium is trivalent or divalent. The properties of some of the halides are listed in Table 29.

TABLE 29

Some properties of titanium halides

Halide	Color	Melting point, °C	Boiling point, °C	Heat of formation, kcal/mole
TiF_4	Colorless	427	284	370
$TiCl_4$	"	-23	136	190.4
$TiCl_3$	Violet	927	Decomposes below bp	170.0
$TiCl_2$	Black	1025	1500	121.5
$TiBr_4$	Yellow	38	230	155
TiI_4	Dark-red	150	377	101
TiI_3	Dark-violet	~1030	Decomposes below bp	~102
TiI_2	Black-brown	~630	~1030	~76

Titanium chlorides. Titanium tetrachloride $TiCl_4$ is the main starting compound for the production of titanium metal. It is a colorless liquid with a density of 1.727. The chloride is produced by the effect of chlorine on titanium dioxide (usually in the presence of carbon) at 700 to 900°.

Titanium chloride hydrolyzes in water or in moist air, with the precipitation of metatitanic acid:

$$TiCl_4 + 3H_2O \rightarrow H_2TiO_3 + 4HCl.$$

This explains the appearance of a dense white smoke when titanium chloride is brought into contact with humid air. Titanium chloride is a

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volatile substance which boils without decomposing at 136°. The heat of evaporation of $TiCl_4$ is -9 kcal/mole.

Two lower chlorides are known: $TiCl_3$ and $TiCl_2$. They are produced by reduction of $TiCl_4$ with hydrogen, titanium, sodium, and other metals, at 600 to 800°.

The lower chlorides tend to disproportionate, i. e., to decompose into compounds in which the valency of titanium is lower and higher than its valency in the starting compound:

$$2TiCl_3 \overset{\text{above } 450^\circ\text{C}}{\rightleftarrows} TiCl_2 + TiCl_4,$$

$$2TiCl_2 \overset{\text{above } 475^\circ\text{C}}{\rightleftarrows} TiCl_4 + Ti.$$

Both lower chlorides are hygroscopic — $TiCl_3$ dissolves in water, while $TiCl_2$ reacts with water with the evolution of hydrogen and the formation of a solution of trivalent titanium. $TiCl_2$ is oxidized in air, sometimes spontaneously bursting into flame.

Titanium iodides. Titanium forms three iodides — TiI_4, TiI_3 and TiI_2 (see Table 29). The higher iodide is produced by the action of iodine vapors on titanium powder at 100 to 200°; the lower iodides are formed by thermal dissociation of TiI_4 at 400 to 1100°. Above 1100° all the iodides decompose into elemental titanium and iodine. This is one of the methods for the production of high-purity titanium.

Titanium fluorides. Titanium fluoride TiF_4 is of no importance, but the complex potassium and sodium fluotitanates K_2TiF_6 and Na_2TiF_6 are used in the production of titanium. They are produced by the addition of sodium or potassium salts to solutions of titanium dioxide in hydrofluoric acid. The solubility of K_2TiF_6 in water at 20° is about 2.2%, that of Na_2TiF_6 6.5%. Both salts crystallize readily from solutions.

Titanium carbides and nitrides (Table 30). Titanium carbide TiC and nitride TiN are very hard, refractory substances with some metallic properties (metallic luster, electrical conductivity). They have the same crystalline structure (face-centered cubic) and form with each other a continuous series of solid solutions.

TABLE 30

The properties of titanium carbide and nitride

Compound	Lattice parameter, Å	Density	Melting point, °C	Heat of formation, kcal/mole	Microhardness, kg/mm²
TiC	4.31	4.93	3140	57.25	2850
TiN	4.23	5.21	2950	80.3	2160

Titanium carbide is formed by heating a mixture of titanium dioxide and carbon at 1900 to 2000°:

$$TiO_2 + 3C = TiC + 2CO.$$

The pure nitride may be produced by the action of nitrogen on titanium powder at 800 to 1000° or by heating $TiCl_4$ in a stream of ammonia:

$$3TiCl_4 + 16NH_3 = 3TiN + 12NH_4Cl + {}^1/_2N_2.$$

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Uses of titanium

Titanium and titanium-based alloys. The interest in titanium, and the resulting development of the titanium industry in 1948 to 1950 were related to the necessity for structural materials combining minimum weight with great strength. The main consumer of such materials is the aircraft industry, in which the saving of one kg on an engine is equivalent to a saving of 8 to 10 kg in the overall weight.

As is evident from Figure 87, titanium-based alloys possess a high specific strength (strength-to-specific gravity ratio). The best modern titanium-based alloys (containing Al, Cr, V, Mo, Sn) have a tensile strength of 120 to 150 kg/mm^2 after heat treatment, which is equivalent to a specific strength of 27 to 33. Alloy steels of the same tensile strength have a specific strength of 15.5 to 19.

At room temperature, titanium-based alloys are only slightly superior to high-strength alloys based on aluminum and magnesium. However, aluminum alloys rapidly lose their strength at 150 to 430° while titanium alloys conserve it. At these temperatures titanium is superior to stainless steel as well.

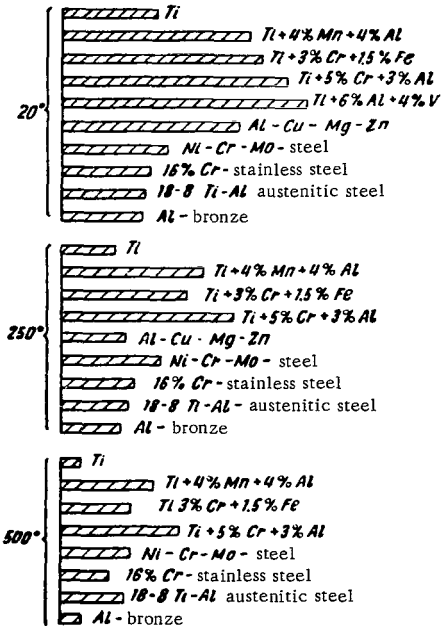

FIGURE 87. Comparison between the strengths of *titanium alloys, steels, and nonferrous metal alloys* (per unit weight).

In the aircraft industry, titanium alloys are used for the manufacture of parts of the fuselage, pistons, connecting rods, valves, and jet-engine parts (compressor discs, turbine blades, rotors, etc.).

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The use of titanium in shipbuilding and the automobile and railroad-car industries is very promising.

In addition to their high strength, titanium and titanium-based alloys possess an increased resistance to corrosion. As a result, they find increasing use in the manufacture of chemical equipment, medical instruments, etc.

Pure titanium (in the form of forged parts, ribbons, and wire), is used in the vacuum-tube industry for the production of anodes, grids, anti-cathodes, X-ray tubes, and other parts. Titanium powder is used in the same field as a getter (gas absorber).

At present, the leading countries in the production of titanium and titanium-based alloys are the USA and the USSR. Titanium is also commercially produced in Canada, United Kingdom, Japan, and other countries. The titanium production in the USA in 1960 to 1962 amounted to about 7000 to 8000 tons per year. As the cost of titanium decreases, there will be an increase in the demand and production volume of this metal.

Titanium in steels. Because of its great affinity for oxygen and nitrogen, titanium is used to deoxidize steel and to free it from dissolved nitrogen (titanium forms with nitrogen a nitride insoluble in the steel). The removal of oxygen and nitrogen from the steel leads to the creation of a fine, dense structure of improved mechanical properties. In addition to the oxygen and nitrogen, titanium also binds sulfur with the formation of a stable sulfide. This prevents the formation of layers of the low-melting eutectic Fe—FeS on the grain boundaries of the steel, which causes hot-brittleness of the steel.

Common brands of steel are deoxidized and freed from nitrogen by the addition of 0.03 to 0.2% titanium, in the form of ferrotitanium (an iron-titanium alloy containing 18 to 25% Ti).

Titanium is used as an additive to manganese, chromium, chromium-molybdenum, and chromium-nickel steels. The addition of titanium to chromium-nickel stainless steels prevents intercrystalline corrosion, which is caused by the precipitation of chromium carbides on the grain boundaries (during welding or tempering of the steel).

Titanium in nonferrous alloys. The addition of titanium to copper or to copper- or aluminum-based alloys improves their physical and mechanical properties and their resistance to corrosion. Cuprotitanium (a copper-titanium alloy containing 6 to 12% Ti) is used for the deoxidation of copper. The strength of aluminum bronze (a copper-aluminum alloy) is increased by the addition of 0.5 to 1.55% Ti. The titanium is added in the form of "alutite"*, containing 40% Al, 22 to 50% Ti, 40% Cu.

Titanium in refractory alloys. Titanium carbide, which is distinguished by its high hardness and refractoriness, is a component of hard titanium-tungsten tool steels. These alloys contain 10 to 40% TiC, 50 to 85% WC, while the remainder is cobalt.

These alloys are effectively employed in the production of steel-cutting tools, and are of great economic importance.

Titanium carbide is also a component of scale-resistant refractory alloys which are used for the production of gas-turbine parts for jet engines.

Titanium dioxide. The most important use of titanium dioxide is the production of a white pigment — titanium white. Titanium white has good

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* [Russian trade name for a titanium master alloy.]

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covering power and is nonpoisonous, which makes it superior to lead whites. Titanium dioxide is used in painting machine parts and ships, is added to the rubber compositions which it is desired to color white, is used for imparting a dull finish to silk, is added as an opacifier to paper pulp, and is used in the production of glazes and enamels.

The total production of titanium pigments in the Western countries was 400,000 and about 1,000,000 tons in 1955 and 1960 respectively.

The high dielectric constants of the various crystalline forms of titanium dioxide (anatase 78, rutile 173 to 180) and of barium titanate is the reason for the use of these compounds in the production of solid dielectrics for condensers, radio parts, and high-frequency furnaces.

Natural titanium dioxide (rutile) or the technical grade dioxide are used as components of the coating of electrical welding electrodes.

39. MINERALS, ORES, AND ORE CONCENTRATES

Titanium is the tenth element in order of abundance. Its concentration in the Earth's crust is 0.61% by weight. It is one of the most abundant metals, following aluminum, iron, and magnesium. Titanium is encountered in all igneous and sedimentary rocks, as well as in the soil, peat, coal, many plants, and the blood and bones of animals.

The position of titanium in the periodic table explains, to a certain extent, its geochemical link to other elements in nature. Figure 88 shows the so-called "geochemical star" of titanium, in which the arrows indicate the attraction of various elements (which are neighbors of titanium in the periodic table) in the ore towards the titanium. Less strong bonds are designated by dotted lines.

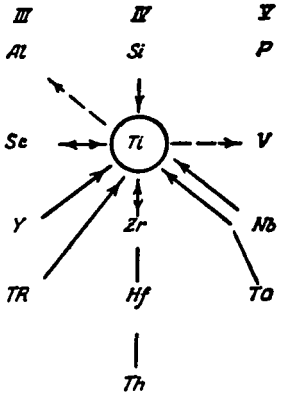

FIGURE 88. The "geochemical star" of titanium, according to Fersman.

In the Earth's crust titanium is present as the dioxide or as titanates — salts of titanic acid. The element tends to form complex anions, comprising niobium, silicon, and zirconium. Thus, in addition to the simple titanates, there are complex titanoniobates, silicotitanates, etc.

There are about 70 known titanium minerals. The ones of greatest commercial importance are rutile, ilmenite, perovskite, and sphene, which are true titanium minerals.

Rutile, anatase and brookite are allotropic modifications of titanium dioxide. Ferrous iron is present as an impurity. Of the three minerals, rutile is of commercial importance. Rutile has a diamond-metallic luster, is transparent, and its color is red-brown or, occasionally, yellowish, bluish, violet, or black. Its density is 4.18 to 4.28.

Large rutile deposits are rare. Rutile deposits have been found in Canada, Brazil, and Australia. The largest amounts of rutile (up to

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70 to 80% of the total or about 70,000 tons) is mined in Australia. Rutile concentrates contain 90 to 95% TiO_2.

Ilmenite (iron metatitanate $FeTiO_3$) is the most common titanium mineral. It was first found in the Ural mountains, in the Ilmenskie mountains. The mineral is brown or black-brown, its density is 4.56 to 5.21. Its chemical formula indicates a TiO_2 content of 52.66%. However, some ilmenites contain 60 to 65% TiO_2. This is attributed to the oxidation of divalent to the trivalent iron as a result of prolonged weathering.

TABLE 31

Approximate composition of some ilmenite concentrates, in %

Chemical composition	USSR			India, Travancore deposits	Norway
	Ural	Irsha	Samotkanskii		
TiO_2	44.0	48.75	60.3*	54.3	42.3
FeO	31.4	45.9	—	26.0	33.9
Fe_2O_3	16.9		25.88	15.5	12.9
SiO_2	1.8	3.3	1.20	1.4	3.5
Al_2O_3	~ 2.5	0.5	2.0	1.1	1.8
Cr_2O_3	—	—	1.36	—	—
MgO	2.76	1.3	0.9	0.85	1.6
MnO	0.72	—	0.85	0.40	0.35
CaO	~ 1.3	1.1	0.17	0.08	0.20
ZrO_2	—	—	~ 0.33	2.18	0.03
V_2O_5	—	—	—	0.20	0.40

* The high TiO_2 content of Samotkanskii concentrates is attributed to the fact that they contain the transformation production of ilmenite which are enriched in TiO_2 (leucoxenes).

In addition to iron oxides, ilmenite may also contain (as impurities) magnesium and manganese since $FeTiO_3$, $MgTiO_3$ and $MnTiO_3$ are isomorphous. Ilmenite is often closely associated with magnetite (Fe_3O_4). Such ores are known as titanomagnetites. In addition, there are ores known as hematitoilmenites, which consist of mixtures of ilmenite and hematite (Fe_2O_3).

Up to 40% of the ilmenite is produced from river and coastal (sea) placers which are formed as a result of the weathering of various ilmenite-containing rocks. The largest ilmenite-bearing placers are found in India, (Travancore). Such placers are also found on the coast lands of Australia, Indonesia, Africa, South America, and the USA. In the USSR, titanomagnetite-bearing sands are found in the areas of Dnepr-Donets and the Black Sea depressions. The placers now being worked contain from one to several dozen kilograms of ilmenite per cubic meter of sand. The sands are often of a complex composition. Thus, sands from Samotkanskii contain rutile, ilmenite, zircon, as well as disthene ($Al_2O_3 \cdot SiO_2$) and staurolite [$Fe(OH)_2 \cdot 2AlSiO_5$] which are valuable sources of aluminum /27/.

Titanomagnetite deposits are an important source of ilmenite. The largest such deposits are found in Canada, the USSR, the Scandinavian countries and Brazil.

Perovskite — calcium titanate, $CaTiO_3$ — contains 58.7% TiO_2 and 41.3% CaO. In some deposits it also contains niobium, yttrium, manganese,

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and magnesium as impurities. Its color is black, red-brown, red, or yellow. Its density is 3.95 to 4.04. Large deposits of perovskite ores have been found in the USSR. The beneficiation of these ores is simple. With increasing consumption of titanium raw materials, perovskite ores will become one of the most important sources of titanium.

Sphene or titanite (calcium titanosilicate $CaO \cdot TiO_2 \cdot SiO_2$) contains 38.8% TiO_2. A fraction of the CaO may be replaced by FeO and MnO. The mineral has a yellow color, its density is 3.4 to 3.56. Sphene deposits have been found in the USA, Canada, Madagascar, and in many regions in the USSR. The titanium content in sphene is lower than in ilmenite, rutile or pervoskite. However, its utilization may be profitable under certain conditions (combined utilization with other ores — apatite and nepheline).

In addition to the raw materials listed above, complex minerals may also be used as a source of titanium. Loparite and some other titanium-niobium minerals belong to this class.

The TiO_2 content in the ores processed varies within wide limits — from 6 to 35%.

In the beneficiation of ilmenite sands, the heavy minerals, the so-called schlichs (magnetite, ilmenite, rutile, zircon, and others), are extracted first, by gravity methods (wet jigging, screw-type separators, tables). The main methods used for the separation of the schlichs are electrostatic and electromagnetic. If the magnetic permeability of iron is assigned a value of 100, that of magnetite would be 40.2, of ilmenite 24.7, of rutile 0.4, and of silicates less than 0.2. Magnetic separation is used to separate magnetite from ilmenite, and ilmenite from rutile and nonmagnetic heavy minerals.

In the case of the collective concentrate of heavy minerals obtained from the sands of the Samotkanskii deposit, electrostatic separation in conjunction with magnetic separation is successfully employed to produce rutile concentrates (containing up to 95% TiO_2), ilmenite concentrates (containing 60 to 62% TiO_2) and zircon concentrates (up to 67.5% ZrO_2) /27/.

Flotation methods have been recently developed for the extraction of ilmenite.

Magnetic separation is used with success for the beneficiation of titanomagnetite ores impregnated with coarse ilmenite particles (in the form of crystals with a size of 0.1 to 0.2 mm). By using weak magnetic fields an iron concentrate (magnetite), an ilmenite concentrate (the weakly magnetic fraction), and tailings (the nonmagnetic fraction) are obtained.

The approximate composition of ilmenite concentrations is shown in Table 31.

Some titanomagnetites cannot be enriched by mechanical processes, as they consist of a solid solution of TiO_2 in Fe_3O_4. Metallurgical beneficiation — smelting in electrical furnaces with the production of pig iron and Ti-rich slags — may be used in such cases.

40. PRODUCTS OF THE PROCESSING OF TITANIUM CONCENTRATES

Three types of products are obtained directly from the titanium concentrates: titanium tetrachloride, titanium dioxide, and ferrotitanium.

Titanium tetrachloride is the main starting material in the production of metallic titanium. High-purity tetrachloride is required for

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this purpose. Hence, the technical grade titanium chloride obtained in the chlorination of titanium raw materials is subjected to further purification. The purified titanium chloride is a transparent, colorless or light-yellow liquid.

Titanium dioxide is produced in different grades of purity and structure, depending on its intended use.

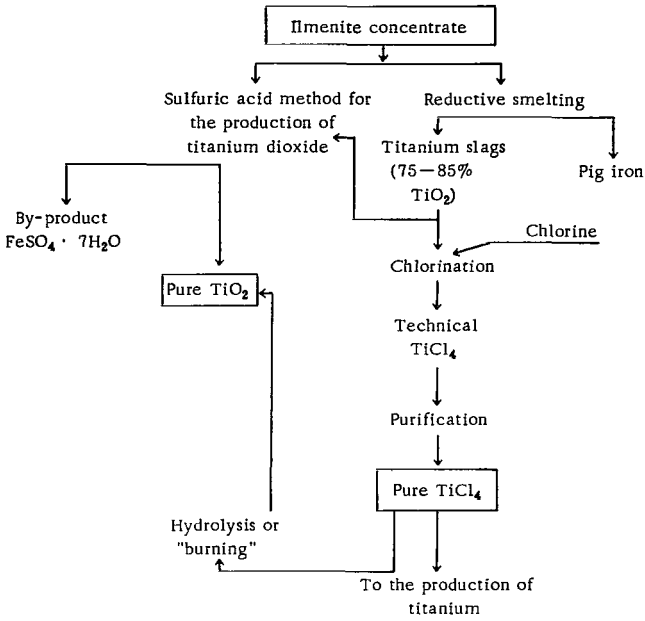

FIGURE 89. General flow sheet of the production of titanium tetrachloride and titanium dioxide from ilmenite concentrates.

Pigment grade titanium dioxide (titanium white) contains from 94 to 98.5% TiO_2 and some oxide admixtures (ZnO, Al_2O_3, SiO_2 and occasionally Sb_2O_3), which are introduced in order to obtain the required structure and physicochemical properties. Some pigment brands have the structure of rutile, others of anatase. The particle size of pigment-grade titanium dioxide must be $\leqslant 1\mu$.

The specifications for titanium dioxide used in metallurgy are only concerned with its chemical purity; its structure is of no importance.

The purest titanium dioxide (containing at least 95.5% TiO_2) is used in the production of carbide-type hard alloys and for the production of titanium metal.

Dioxide containing at least 99% TiO_2 is used for the production of alloys with nonferrous metals (nickel, copper, aluminum), while the dioxide containing at least 97.5% TiO_2 is used for the production of welding-electrode coatings.

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Ferrotitanium is produced from ilmenite concentrates by thermal reduction with aluminum in electrical furnaces. The alloys contain 25 to 30% Ti, 5 to 8% Al, 3 to 4.5% Si; the remainder is iron.

The industrial methods for the production of titanium tetrachloride and titanium dioxide from the main raw material, ilmenite concentrates, are described below.

A flow sheet of the processing of ilmenite concentrates is shown in Figure 89. It will be seen that titanium chloride is produced by chlorination of titanium slags (75 to 85% TiO_2) formed in the smelting of ilmenite concentrates. Two methods are used for the production of titanium dioxide: a) direct decomposition of ilmenite concentrates (or titanium slags) with sulfuric acid followed by precipitation of metatitanic acid from the sulfate solution; b) hydrolytic decomposition (or "burning") of titanium tetrachloride.

41. REDUCTIVE SMELTING OF ILMENITE /5, 15, 25, 28/

Ilmenite concentrates contain 42 to 60% TiO_2 and 40 to 48% $FeO + Fe_2O_3$ (see Table 31).

The high concentration of iron interferes with the production of titanium chloride from ilmenite. A large amount of chlorine is consumed in the formation of iron chloride during direct chlorination of the concentrates. Moreover, there are difficulties in finding use for the large amounts of the iron chloride formed.

The iron is separated by selective reductive smelting of ilmenite, with the formation of pig iron and titanium slags (80 to 87% TiO_2). In this process, the separation of titanium and iron is based on the large difference between the stabilities of their oxides.

Titanium slags have a high melting point (above 1500°) and a considerable viscosity. For this reason, iron ores with a high titanium content (e.g., titanomagnetites) are usually not smelted in blast furnaces. However, electric arc furnaces may be used for the reductive smelting of ilmenite concentrates.

The following main reactions take place during the reduction of ilmenite by carbon at various temperature ranges:

$$\left.\begin{aligned} FeTiO_3 + C &= Fe + TiO_2 + CO \\ 3TiO_2 + C &= Ti_3O_5 + CO \end{aligned}\right\} \text{ up to } \sim 1240°$$

$$2Ti_3O_5 + C = 3Ti_2O_3 + CO \text{ at } 1270 \text{ to } 1400°$$

$$Ti_2O_3 + C = 2TiO + CO \text{ at } 1400 \text{ to } 1600°$$

The intermediate oxide Ti_3O_5 and the oxide Ti_2O_3 may dissolve the ferrous oxide and the ilmenite, and form solutions with TiO_2 and the monoxide TiO. These reactions lead to the formation of complex compounds which crystallize when the slags solidify. The most important of these substances is anosovite, whose composition can be expressed by the general formula $m[(Mg, Fe, Ti)O \cdot 2TiO_2]n[(Al, Fe, Ti)_2O_3 \cdot TiO_2]$. The formula shows that titanium exists in anosovite in various valencies — Ti^{4+}, Ti^{3+}, and Ti^{2+}.

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In addition to anosovite, the lower titanium oxides and the solid solution of ilmenite in Ti_2O_3, the slags may also contain titanium oxycarbonitride Ti(C, O, N). This is a solid solution of titanium carbide, nitride, and monoxide (TiC — TiN — TiO). The oxycarbonitride is formed at temperatures above 1600° in the presence of an excess of carbon. The lower oxides, and especially titanium oxycarbonitride, cause an increase in the melting point and the viscosity of the slags. The melting point and viscosity of the slags may be reduced by the addition of fluxes such as calcium, magnesium, and aluminum oxides. However, this results in a decrease of the TiO_2 content of the slags and causes increased consumption of chlorine, because of the formation of calcium, magnesium, and aluminum chlorides. Hence, the tendency is to carry out the smelting with the addition of as little flux as possible, or altogether without it.

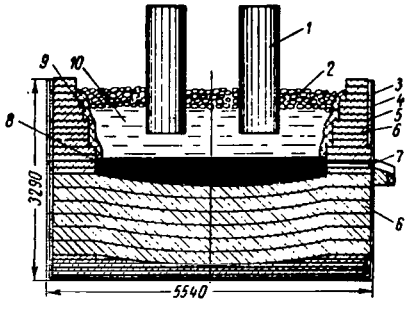

FIGURE 90. Diagram of an electric arc furnace for the smelting of slags.

1 — electrodes (the third electrode is not shown); 2 — charge; 3 — steel jacket; 4 — asbestos-cement sheet; 5 — magnesite grit; 6 — magnesite refractory bricks; 7 — tapping hole; 8 — pig iron; 9 — slag hardened on the walls; 10 — slag.

The reductive smelting is carried out in three-phase electric arc furnaces (5000 to 10,000 kVa), similar to the ones used in the production of ferroalloys such as ferrochromium.

A diagram of a 5000 kVa furnace is shown in Figure 90 /25/. The bath is a cylindrical jacket lined with magnesite refractories. The bath walls have descending steps. The tapping hole is at a height of 310 mm above the lower point of the hearth. In the working zone of the furnace the walls have a thickness of 690 mm and the hearth 1380 mm. Above the bath there are three graphitized electrodes (500 mm in diameter) which are held in cooled clamps and are connected to a displacing device.

A layer of slag (about 0.5 m thick) is allowed to harden preliminarily on the lining of the furnace in order to protect it against rapid attack by the corrosive titanium slags. A thick layer of pig iron (0.5 m or more) is always left on the hearth in order to prevent attack by the slag.

The smelting is carried out with a covered charge hole, i. e., with the arc covered by the charge (the electrodes are immersed deep inside the charge). Coke or anthracite, crushed to a particle size of 3 to 4 mm, is used as the reducing agent. The components of the charge (concentrate, coal) pass from the storage bins through metering trolleys into three furnace bins which are positioned above the furnace. From the bins the charge on moving trays is charged into the space between the electrodes and along the furnace walls.

For the best utilization of the reducing agent and in order to reduce dust formation and the consumption of electrical energy, it is most convenient to use a pelletized charge. However, this causes difficulties because of the sintering of the pellets and their cementation by the boiling melt, which reduces the gas-permeability of the charge. As a result, in industrial practice the smelting is carried out on a mixed charge, i. e., a

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mixture of pelletized and pulverized charge. The ratio of pelletized to pulverized charge depends on the type of titanium concentrate taken. The pulverized charge content varies between 20 and 50%. The pellets are prepared in roller presses, using sulfite-pulping liquor as the binder.

Various smelting conditions are used. One of these, used in a batch process, is described below /5, 25/. The smelting cycle is divided into three stages: fusion of the charge, rapid reduction, and finishing the slags before tapping. The amount of carbon is calculated to produce a slag with a ferrous oxide content of 5 to 6%. Slags with a lower FeO content are fused with difficulty without the addition of fluxes, as they have a high melting point and rapidly solidify. This is attributed to the formation in these slags of titanium carbide or oxycarbide. In slags with a sufficiently high FeO content the oxycarbide reacts with it according to the reaction:

$$TiC \cdot TiO + 3FeO = Ti_2O_3 + CO + 3Fe.$$

The smelting is facilitated by adding to the charge at first only a fraction of the carbon, calculated to produce a low-melting slag (up to 20% FeO). The rest of the carbon is then added gradually, and the reduction is continued in the liquid phase until the FeO content reaches 5 to 6%. The last stage of the smelting — the finishing — has the purpose of melting the slag frozen on the walls and the crowns formed by it. In this stage the electrodes are withdrawn and the furnace operates with an exposed arc.

The slags and the pig iron are tapped periodically through the tapping hole into a common pan lined with chamotte bricks. The temperature of the slag during the tapping is 1570 to 1650°. The pig iron and the slags are allowed to separate into layers, to solidify, and are then separated.

The smelting is carried out at a voltage of 130 to 135 V. The total time for the smelting of a charge of 12 tons is about 4 hours. The consumption of electrical energy is about 3000 kwh per ton of slags.

The smelting of Irsha ilmenite concentrates (see Table 31) by the above method yielded slags with the following composition: 85.7% TiO_2, 6.5% FeO, 5.65% SiO_2, 1.9% Al_2O_3, 3.0% MgO, and 0.75% CaO. The degree of extraction of titanium from the concentrate into the slags was about 95% /5/.

42. REDUCTION OF ILMENITE TO TITANIUM CARBIDE (THE CARBIDIZATION PROCESS)

When a mixture of ilmenite concentrate and carbon is heated to 1900—2000° the ilmenite is reduced yielding titanium carbide and iron (pig iron):

$$FeTiO_3 + 4C \rightarrow TiC + Fe + 3CO.$$

As the pores of the charge contain some nitrogen, the product is, in fact, not the pure carbide but the carbonitride Ti(C,N) (a solid solution of titanium carbide and nitride) or the oxycarbonitride Ti(Ci,N,O). The formation of such products is associated with the fact that the carbide TiC, the nitride TiN, and the monoxide TiO have crystal lattices of the same type with close values of lattice parameters. These compounds form a continuous series of solid solutions.

After the cake has been ground, most of the iron is extracted from titanium carbide by electromagnetic separation. Titanium carbide (or, more accurately, titanium oxycarbonitride) obtained is forwarded to chlorination.

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The reaction of the carbide (or oxycarbonitride) with chlorine is a rapid reaction taking place at a relatively low temperature (300—400°) and is accompanied by the evolution of a considerable amount of heat, which is sufficient to support the chlorination process. This is the main advantage of the chlorination of titanium carbide over the chlorination of rutile or titanium slags.

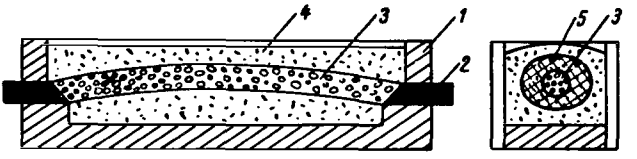

FIGURE 91. Diagram of a core furnace:

a—longitudinal section; b—cross section; 1—refractory brick lining; 2—graphite electrodes; supplying the current to the core; 3—granulated coke core; 4—charge positioned around the core; 5—reacted part of the charge.

It has been reported that in some plants the carbidization of ilmenite is a stage preliminary to the chlorination. According to one report, the carbidization is carried out in resistance furnaces resembling the ones used for the production of silicon carbide (carborundum). Such furnace is shown schematically in Figure 91. It is pan-shaped, and its end walls are connected to current terminal electrodes. A core consisting of coke particles, which serves as the heating element, is positioned between the electrodes. The charge is poured around the core. The charge layers adjacent to the core are heated to the required temperature (1900 to 2000°). The temperature decreases with increasing distance from the core, and no carbidization takes place in the outer layers of the charge adjacent to the walls. These layers serve as thermal insulation, and are returned to be mixed with the fresh charge.

The consumption of electrical energy is about 5000 kwh per ton of cake.

After grinding to a particle size of -0.30 mm and magnetic separation, oxycarbonitride of the following composition is obtained: 68.1% Ti, 2% Fe, 9.3% C, and 0.4% N.

43. PRODUCTION OF TITANIUM TETRACHLORIDE

Reaction mechanism

Titanium dioxide reacts with chlorine; the reaction is endothermic:

$$TiO_2 + 2Cl_2 = TiCl_4 + O_2 - 45 \text{ kcal}.$$

This reaction is very slow even at 800 to 1000°. A reaction rate high enough to be of practical importance is obtained at 700 to 900° in the presence of a reducing agent — carbon. The carbon combines with the oxygen, yielding CO, CO_2 and some phosgene $COCl_2$, and all the chlorination reactions are exothermic:

$$TiO_2 + 2Cl_2 + C \rightleftarrows TiCl_4 + CO_2 + 49 \text{ kcal}; \quad (1)$$

$$TiO_2 + 2Cl_2 + 2C \rightleftarrows TiCl_4 + 2CO + 78 \text{ kcal}; \quad (2)$$

$$TiO_2 + 4Cl_2 + 2C \rightleftarrows TiCl_4 + 2COCl_2 + 62 \text{ kcal}. \quad (3)$$

The equilibrium pressure of phosgene ($COCl_2$) at 600 to 800° is extremely low, and reactions (1) and (2) are predominant (see Table 32).

The relative amount of CO in the gas mixture increases with increasing temperature. At 800° and above the chlorination (under equilibrium

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conditions) should proceed mainly according to reaction (2), i. e., with the formation of carbon monoxide. Since reaction (2) yields two molecules of CO while reaction (1) yields one molecule of CO_2, increasing the chlorination temperature increases the consumption of carbon per mole of $TiCl_4$ and increases the total volume of the gaseous phase (and thus reduces the $TiCl_4$ concentration in the gas mixture).

TABLE 32

Equilibrium composition of the gaseous phase in the chlorination of titanium dioxide by chlorine in the presence of carbon

(According to Godnev and Pamfilov)

Temperature, °C	Partial pressure, (equilibrium), atm.				
	CO	CO_2	$TiCl_4$	$COCl_2$	Cl_2
600	0.175	0.370	0.455	$5.7 \cdot 10^{-7}$	$1.47 \cdot 10^{-5}$
800	0.600	0.047	0.353	$4.9 \cdot 10^{-7}$	$7.4 \cdot 10^{-5}$

In practice, no equilibrium is reached in the chlorination. For this reason, even at 900° the gases contain CO_2. The $CO : CO_2$ ratio in the gas mixture depends on the method and conditions of chlorination.

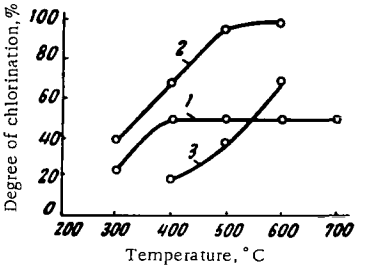

FIGURE 92. Degree of chlorination (by chlorine) after one hour at various temperatures.

1 — TiO; 2 — TiO + C; 3 — TiO_2 + C.

At any given temperature, the rate of chlorination of titanium slags is higher than that of rutile concentrates. This is attributed to the fact that titanium salgs contain lower titanium oxides and occasionally titanium oxycarbide, whose reaction with chlorine is more vigorous than the reaction between chlorine and titanium dioxide. Thus, titanium monoxide reacts with chlorine at an appreciable rate at 300° in the absence of carbon, according to the equation /17/

$$2TiO + 2Cl_2 = TiCl_4 + TiO_2.$$

At 500°, in the presence of carbon, the chlorination of TiO is 2 to 2.5 times faster than that of TiO_2 (Figure 92). This is explained by the fact

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that the active titanium dioxide formed in the reaction is rapidly chlorinated in the presence of carbon. It is probable that the formation of active titanium dioxide is the first stage in the chlorination of Ti_2O_3 and Ti_3O_5 as well.

In addition to titanium oxides, the material to be chlorinated contains various amounts of the oxides of iron, manganese, calcium, magnesium, aluminum, silicon, vanadium, and some other elements. Of these elements, Fe, Al, Si, V, Cr, Ta, and Nb form volatile chlorides (see p. 177). Free silicon reacts slowly with chlorine in the presence of carbon at 800 to 900°, but the silicates are chlorinated rapidly.

Procedures

Three methods of chlorination are used at present in industry: *chlorination of pelletized charge in a stationary layer, chlorination in* molten salts, and chlorination in a fluidized bed.

Chlorination in a stationary layer. The process is carried out in electrical shaft furnaces. The chlorination is preceded by preliminary operations — grinding of charge components, mixing, briquetting, and coking of the briquettes /1, 30/.

The amount of carbon added to the charge depends on the composition of the material to be chlorinated and the process temperature. Assuming that at 800 to 900° the chlorination proceeds with the preferential formation of CO, the theoretical consumption of carbon by a charge containing 80% TiO_2 is 24 kg per 100 kg slag. This does not allow for the fact that a part of the titanium in the slags is in the form of lower oxides. In practice, the charge contains 20 to 25% of pulverized petroleum coke.

Sulfite lyes*, coal pitch, and other materials are used as binders to produce strong pellets.

The briquetting technology is the same as for niobium (see Chapter III); the type of shaft furnace used for the chlorination and its operation are also the same (see Figure 56).

The stoichiometric amount of chlorine needed for the production of one ton of $TiCl_4$ is 0.75 ton. In practice, 0.85 to 0.90 ton of chlorine is spent in the chlorination of slags per ton of chloride, because of the chlorine *lost through the formation of chlorides of other elements.*

Sodium, calcium, magnesium and manganese chlorides, which have high boiling points, form a liquid melt which flows downwards through the pores of the charge and the coal packing on the hearth and is periodically tapped into the ladle. The vapor-gas mixture, containing carbon monoxide and dioxide, $TiCl_4$, volatile chloride impurities ($FeCl_3$, $AlCl_3$, $SiCl_4$, $VOCl_3$, CrO_2Cl_2, etc.) and a small amount of excess chlorine is vented through a tube in the upper part of the furnace into a dust-collecting and condensation system.

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* These are the waste liquors of cellulose pulping. They contain organic substances. The concentrated lyes have binder propertes.

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The specific output of chlorinators with a stationary layer of pelletized charge (in the chlorination of titanium slags) is about 70 to 100 kg $TiCl_4$ per square meter of furnace cross section per hour. The degree of extraction of titanium from the slags to form the technical grade $TiCl_4$ is about 83 to 85%.

The $CO : CO_2$ weight ratio in the vapor-gas mixture at the exit from the shaft furnace ranges from 5 : 1 to 8 : 1 depending on the temperature conditions and the height of the charge layer. In the presence of an inflow of air, the gas mixture becomes explosive. To prevent the inflow of air, an overpressure of 3 to 5 mm Hg is maintained at the outlet of the shaft furnace.

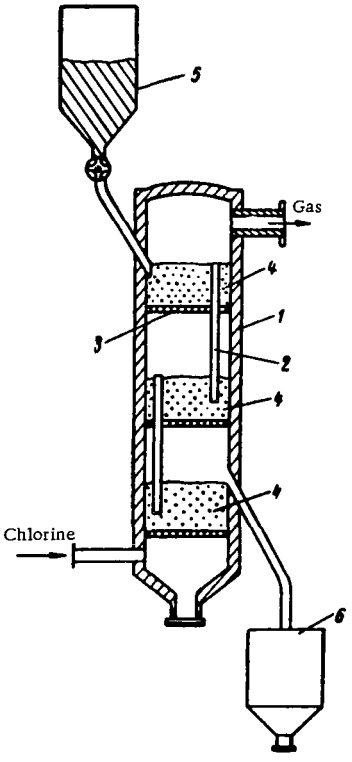

FIGURE 93. Diagram of a three-chamber fluidized-bed chlorinator.

1—stack; 2—overflow, for the passage of material from higher to lower chamber; 3—dispersing grating; 4—fluidized bed; 5—storage bin; 6—collector for residues (nonchlorinated material and nonvolatile chlorides).

In shaft furnaces with a productivity of 25 tons $TiCl_4$ per day, most of the heat (62.0%) comes from the chlorination reaction. The heat furnished by the electrical elements amounts to 38%, corresponding to a consumption of 7.84 kwh per ton $TiCl_4$. The vapor-gas mixture entrains 66.2% of the heat from the furnace. Heat losses through the lining and the jacket of the furnace account for 33.8% of the heat, which is nearly equal to the amount supplied by electrical heating /32/.

Chlorination in the melt /30/. This method for the chlorination of titanium slags was proposed in the USSR by an engineer, Solyakov. The chlorination is carried out in a bath of molten potassium and sodium chlorides, in which the charge (a mixture of ground slag and coke) is introduced. The charge may be introduced through a charging tube in the roof of the chlorinator, with the aid of dry compressed air or nitrogen. The chlorine is fed to the lower part of the chlorinator and is dispersed through a grid fitted in the interior, or by means of special nozzles.

At 700 to 800° the chlorination in the melt proceeds rapidly. The titanium chloride together with the volatile chloride impurities ($SiCl_4$, $AlCl_3$, $FeCl_3$) passes into a condensation system, while the nonvolatile chlorides ($MgCl_2$, $CaCl_2$, etc.) remain in the melt. After considerable amounts of the nonvolatile chlorides have accumulated, there is a change in the properties of the melt, and especially in its viscosity, which interferes with its saturation by chlorine. For this reason, the melt is periodically tapped out of the chlorinator and a fresh batch of the molten salts is added.

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In the chlorination, the required melt temperature is maintained by the heat evolved in the exothermic reactions. The excess heat is removed by means of cooled ducts (made of graphite plates) mounted on the walls of the chlorinator.

As compared with the chlorination of pelletized charges in electrical shaft furnaces, chlorination in melts has the advantages of not requiring a pelletizing operation, of a higher output of the chlorination apparatus, and of a lower dust content in the vapor-gas mixture.

Anodic chlorine (the gas from the electrolytic production of magnesium, consisting of a mixture of chlorine and air — 70% Cl_2, ~ 25% N_2, and ~ 6% O_2) may be used for the chlorination, instead of pure chlorine. This reduces considerably the cost of titanium chloride.

Chlorination in a fluidized bed /30/. Short communications have been published on the chlorination of titanium slags or rutile concentrates in a fluidized bed. Some idea of fluidized bed processes was given in the chapter "Molybdenum". Fluidized-bed chlorination equipment has the important advantage of permitting a continuous process to be carried out; the output is high. The chlorinators are cylindrical stacks lined with dense Dinas bricks; in the lower part of the stack there is a grating (hearth) serving to disperse the chlorine fed to the apparatus.

The charge, which is a mixture of crushed slag (or rutile) and coke is fed into the fluidized bed with the aid of an air-tight feeder or with the gas stream passed over the surface of the grating. For best utilization of chlorine, it is advisable to use a chlorinator consisting of several chambers placed one over the other (i. e., to mount several gratings in the stack, with a "fluidized bed" of the material on each of them). The fresh charge is fed to the upper chamber, in which it is partially chlorinated by the chlorine coming from below, and from there it passes through an overflow tube into the chamber beneath (Figure 93).

It is very important to select the optimum particle size of the slag (or rutile) to be chlorinated and of the coke, in order to prevent preferential entrainment of one of the components from the charge bed.

In the chlorination of titanium slags, difficulties are caused by the presence of unusually high amounts of calcium, magnesium and sodium oxides which yield relatively low-melting nonvolatile chlorides ($CaCl_2$, $MgCl_2$, NaCl); these collect in the fluidized bed and may cause sintering of the particles and settling of the bed. In such cases, the working temperature of the layer must be maintained at 600°, which reduces the output of the installation. The chlorination of rutile concentrates may be carried out at 900 to 1000°.

The output of fluidized-bed chlorinators ranges from 200 to 500 kg $TiCl_4$ per square meter of hearth per hours, depending on the chlorination temperature; this is much higher than the output of electrical shaft furnaces.

Dust collection and condensation system

The dust collection and condensation system usually consists of d u s t c h a m b e r s (serving to separate the dust particles mechanically entrained from the furnace, and to settle the iron chloride), c o n d e n s e r s

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for the $TiCl_4$, and sanitation scrubbers, for the absorption of the excess chlorine.

A diagram of the condensation system was shown in Chapter III (Figure 57).

The bulk of the dust and the iron chloride are trapped in a dust chamber, with walls cooled by a stream of air passed through the jacket. The gas temperature at the exit of the dust chamber is maintained at 160 to 180°. The vapor-gas mixture coming out of the dust chamber still contains a substantial amount of dust. Accordingly, the condensation of titanium chloride is carried out most conveniently in spray condensers, in which cooled titanium tetrachloride is used as the spray liquid (see Figure 57). The slurry from the irrigated condenser passes through an intermediate collector into a thickener for the separation of slimes. Part of the chloride is withdrawn from the intermediate collector and is used for irrigation. The clarified chloride from the thickener flows into collector tank for technical grade chloride. The thickened pulp is sent to an evaporator, to remove titanium tetrachloride /30/.

The gases issuing from the spray condenser still contain some titanium chloride. It may be trapped in tubular condensers cooled by brine ($CaCl_2$ solution) at -10 to 15°. From there the gases pass through a sanitation scrubber sprayed with lime water (for the absorption of chlorine and hydrochloric acid vapors) and are vented to the atmosphere.

The pipelines of the condensation system may be occasionally clogged by a mixture of iron chloride, titanium oxychloride and dioxide. The last two compounds are formed in the reaction of $TiCl_4$ with water vapor:

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl,$$
$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl.$$

Hydrochloric acid is also formed in these reactions, with resultant corrosion of steel condensers and pipelines. The moisture may enter the furnace or the condensation system together with the air or with the pellets if they are fed to the furnace while cold and with moisture adsorbed on their surface.

The condensation system may be simplified if the iron chloride and the other solid chloride are previously separated by passing the vapor-gas mixture issuing from the dust chamber through a column packed with granular sodium chloride, in which the temperature is maintained at 350 to 450°. The iron and aluminum chlorides form with NaCl eutectic mixtures of low melting point which flow downwards and are periodically tapped /31/. The solid particles may also be separated from the vapor-gas mixture by installing fiber-glass bag filters, in which the temperature is maintained at 200 to 250°.

The total degree of extraction of the titanium with the technical chloride in the chlorination of titanium slags is 90 to 93% .

44. PURIFICATION OF TECHNICAL GRADE TITANIUM CHLORIDE

Technical titanium tetrachloride contains a number of impurities, both dissolved and as a fine mechanical suspension.

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Gases (N, Cl) and several chlorides $SiCl_4$, $SnCl_4$, $VOCl_3$, CrO_2Cl_2, $AlCl_3$, titanium oxychloride $TiOCl_2$, $NbCl_5$, and $TaCl_5$ are present in a dissolved state. The main impurities suspended in titanium chloride are iron chloride, titanium dioxide, and fine carbon particles. The solubility of $FeCl_3$ in $TiCl_4$ is very low: 0.043% at 110° and 0.003% at 40°. The solubility of $AlCl_3$, $TaCl_5$, and $NbCl_5$ is substantial, as is evident from Table 33.

TABLE 33

Solubility in titanium tetrachloride, %/19/

Temperature, °C	$TaCl_5$	$NbCl_5$	$AlCl_3$
18	0.40	0.45	0.26
55	—	2.4	1.1
80	—	—	3.8
106	10.0	12.2	—

Silicon tetrachloride and titanium chloride form a continuous series of liquid solutions (Figure 94).

The solubility of titanium oxychloride $TiOCl_2$ in $TiCl_4$ at various temperatures is shown in Figure 95.

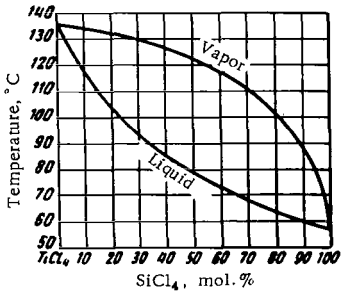

FIGURE 94. Phase diagram of the system $TiCl_4$—$SiCl_4$.

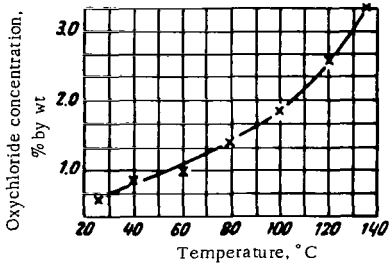

FIGURE 95. Solubility of titanium oxychloride $TiOCl_2$ in $TiCl_4$, as a function of the temperature.

The mechanical impurities are separated from the titanium chloride by filtration through porous earthenware filters or through a layer of activated carbon. In the latter case, part of the dissolved chlorine is also adsorbed from the solution.

After filtration, technical grade titanium chloride has the following composition: 97 to 99% $TiCl_4$, 0.2 to 0.5% Si, 0.02 to 0.002% Fe, 0.1 to 0.03% Cl, 0.06 to 0.2% V, and some Al, Cr, and other elements.

Most of the impurities are removed from the chlorides by the rectification method, which is based on the different boiling points of the chlorides. The boiling points of the chlorides are tabulated below (in °C):

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$TiCl_4$	136	$TaCl_5$	239
$VOCl_3$	127	$NbCl_5$	254
$SiCl_4$	58	$NbOCl_3$	400
CrO_2Cl_2	116,7		(sublimates)
VCl_4	164	Al_2Cl_6	180
$FeCl_3$	319	$SnCl_4$	113

Some impurities, e.g., vanadium oxychloride, are difficult to remove by rectification since $VOCl_3$ and $TiCl_4$ have close boiling points. Therefore, $VOCl_3$ is preliminarily reduced to the less volatile lower chloride. Copper powder is used as the reducing agent. When titanium tetrachloride is mixed with copper powder, the oxychloride is reduced in the reaction:

$$VOCl_3 + Cu \rightarrow VOCl_2 + CuCl.$$

Some VO_2 is also formed. It is most probable that copper powder also reduces the chromium oxychloride and tin chloride (present as impurities) to the lower chlorides.

The presence of aluminum chloride (which is very corrosive) in titanium chloride before rectification is undesirable. To separate aluminum chloride, a small amount of water equal to the amount required for the formation of aluminum oxychloride: $AlCl_3 + H_2O \rightarrow AlOCl + HCl$, is added to the titanium chloride. The precipitate formed (AlOCl) is separated by filtration.

In some plants, vanadium is removed by reduction with hydrogen sulfide /1/. As a result, vanadium is precipitated as the sulfide. In one procedure, H_2S is passed for 4 to 6 hours through a vat containing 2000 kg of $TiCl_4$ at 90°. Hydrogen sulfide is fed in slowly (at a rate of 0.45 kg/hr) from steel cylinders, as its solubility in the titanium tetrachloride is low. The precipitates formed readily settle and are easily separated by filtration.

Purification by rectification. Rectification is a process in which the components of a homogeneous liquid mixture are separated in columns; it is based on the interaction of countercurrent flows of vapors and liquid (formed by the condensation of the vapor) along the column.

We shall discuss here the rectification process in the case of a mixture consisting of two components, one with a lower boiling point (LB) and the other with a higher boiling point (HB).

Let us visualize a packed column, with the vapor mixture from the pot entering the bottom of the column and a liquid consisting of the almost pure LB fed to the upper part. As the vapors come into contact with the descending liquid they transfer to it a part of their latent heat and a fraction of the vapors condenses, while a fraction of the liquid is vaporized. The HB condenses perferentially from the vapor phase while the LB evaporates preferentially from the liquid. Hence, the descending liquid becomes enriched with HB while the ascending vapor becomes enriched with LB. As a result, the vapors at the issue from the column consist of almost pure LB. The LB component enters a condenser (the so-called dephlegmator). A fraction of the condensate is used to irrigate the column (this fraction is known as the phlegm); the rest is collected in the distillate collector. The HB remains in the pot.

In order to obtain a satisfactory separation of the components in the column, it is necessary to provide for the largest possible contact area

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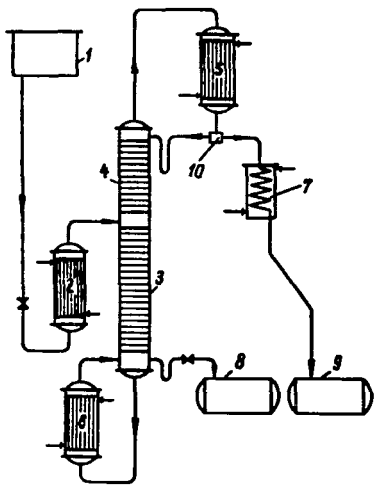

FIGURE 96. Diagram of a continuous rectification installation.

1—pressure tank with $TiCl_4$; 2—heater; 3—stripping section of the rectification column; 4—rectifying section of the column; 5—dephlegmator; 6—boiler; 7—condenser; 8—pot residue collector; 9—distillate collector; 10—flow-rate adjustment valve for the distillate.

between the vapors and the descending phlegm. This is achieved by packing the column, or by mounting a number of bubble-cap, sieve, or meshed trays along its height. Each tray is covered by a layer of liquid; the vapors bubble through the opening in the column and through the liquid on it. Part of the liquid flows down through the openings (or overflow tubes) of one tray onto the tray beneath it.

The rectification may be carried out either batchwise or continuously. A diagram of a continuous rectification column is shown in Figure 96. Continuous rectification columns have two sections — a lower (stripping) and an upper (rectifying) section. The starting mixture is fed to the upper part of the stripping section. There it comes into contact with the vapors whose initial composition is similar to that of the pot residue (HB). As a result the LB is extracted (stripped) from the mixture. In the upper section the vapors coming from the stripping section of the column come into contact with the descending liquid (the phlegm) whose initial composition is the same as that of the distillate (pure LB). As a result the vapors are enriched (rectified) with LB. The vapors used to feed the column are produced by repeated evaporation of the pot residue (HB) in the evaporator, while the phlegm is produced by condensation of the vapors in the reflux condenser.

The ratio of the amount of phlegm (the distillate returned to irrigate the column) to that of the distillate taken out of the column is known as the reflux ratio. It indicates how many kg-moles of distillate must be returned to the column in order to collect one kg-mole of distillate.

The purification of titanium tetrachloride by rectification is carried out in stainless steel columns with perforated trays (or trays with slit-shaped perforations) in two stages. In the first stage silicon tetrachloride is removed by maintaining a temperature of 58° in the upper part of the column (the boiling point of $SiCl_4$). The pot residue ($TiCl_4$ containing the high-boiling chlorides and oxychlorides as impurities) enters the second column in the top section of which a temperature of 136° (the boiling point of $TiCl_4$) is maintained. The distillate consists of pure titanium chloride. Impurities such as chlorides with a higher boiling point (AlOCl, $FeCl_3$, $NbCl_5$, etc., as well as titanium oxychloride $TiOCl_2$) are separated out. Purified titanium chloride is a transparent, colorless or slightly yellowish liquid in which the impurity content is close to the sensitivity limit of spectroscopic analysis. The concentrations of the most common impurities such as Al, V, Cr, Cu, Si, Mn, Ta, Nb, and Zr range from 10^{-5} to 10^{-3}% (of each impurity).

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The degree of extraction of titanium (yield of purified chloride from the technical tetrachloride) purified chloride is 95%.

45. PRODUCTION OF TITANIUM DIOXIDE

The sulfuric acid method /4/

The bulk of the titanium dioxide produced from ilmenite concentrates is prepared by the sulfuric acid method which comprises the following stages:

1) decomposition of the concentrate with sulfuric acid;
2) removal of iron from the solutions;
3) hydrolytic precipitation of metatitanic acid from the sulfate solutions;
4) ignition of the precipitate accompanied by the formation of titanium dioxide.

This method ensures a high degree of extraction of titanium into the final product, through the use of a single reagent — sulfuric acid.

Decomposition of the concentrate. The following reactions take place in the decomposition of ilmenite concentrates with sulfuric acid:

$$FeTiO_3 + 3H_2SO_4 = Ti(SO_4)_2 + FeSO_4 + 3H_2O; \quad (1)$$
$$FeTiO_3 + 2H_2SO_4 = TiOSO_4 + FeSO_4 + 2H_2O. \quad (2)$$

Hence, the solution may contain both Ti^{4+} and TiO^{2+} ions, but TiO^{2+} ions are usually predominant. Ferric oxide, which is always present in the concentrates, dissolves with the formation of $Fe_2(SO_4)_3$. All the reactions involved in the dissolution are exothermic.

In industrial practice technical grade concentrated sulfuric acid (either oil of vitriol — 92 to 94% H_2SO_4, or oleum — concentrated H_2SO_4 containing up to 20% dissolved SO_3) is used for the decomposition. Since the decomposition reactions are exothermic, it is sufficient to heat the acid — ground concentrate mixture to the temperature at which rapid decomposition begins (125 to 135°) and the reaction then proceeds vigorously, the temperature of the mixture rises to 180 to 200°, and the reaction is completed within 5 to 10 minutes. The decomposition product is the so-called "melt" consisting mainly of fine crystalline titanyl sulfate ($TiOSO_4 \cdot H_2O$), ferric sulfate, and some sulfuric acid. The decomposition is carried out either as a batch or as a continuous process.

The apparatus for the batch process is a steel tank with a conical bottom, lined with two layers of acid-resistant (diabase) plates. As a result the apparatus may be used both for the decomposition (which does not require a protective lining) and for the subsequent leaching of the melt with water.

The continuous decomposition of ilmenite may be carried out in an apparatus consisting of a heated screw-conveyer mixer into which is fed the concentrate mixed with sulfuric acid.

Removal of iron from the solution. The decomposition of ilmenite by sulfuric acid yields solutions containing 110 to 120 g/l of TiO_2 (as titanyl sulfate $TiOSO_4$ and the normal titanium sulfate) and iron sulfates ($FeSO_4$ and $Fe_2(SO_4)_3$), and 200 to 240 g/l of active H_2SO_4*.

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* The active H_2SO_4 is the total amount of the free acid and the acid bound to the titanium sulfates.

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The bulk of the iron must be removed from the solution prior to the hydrolytic precipitation of the titanic acid, in order to prevent contamination of the precipitate.

In order to remove the iron from the solution, the trivalent iron is reduced to the divalent state, and ferrous sulfate is crystallized (as $FeSO_4 \cdot 7H_2O$) by utilizing the considerable decrease in the solubility of $FeSO_4$ accompanying the cooling of the solution. The solubility of $FeSO_4$ $7H_2O$ in a solution containing 120 to 140 g/l TiO_2 and 240 g/l H_2SO_4 is (the values are converted to Fe concentration in the solution):

Temperature, °C	30	20	14	10	5	0	-6
Fe content, g/l.....	88	70	48.5	43	35	25	14

The reduction is effected by introducing iron turnings into the solution: $Fe_2(SO_4)_3 + Fe = 3FeSO_4$. The reduction of Fe^{3+} to Fe^{2+} is completed when the solution turns violet; this is caused by the reduction of part of tetravalent titanium to the trivalent titanium sulfate:

$$2TiO(SO_4) + Fe + 2H_2SO_4 = Ti_2(SO_4)_3 + FeSO_4 + H_2O.$$

This reaction begins only after the quantitative reduction of the trivalent iron.

During the decomposition and leaching in batch equipment, the iron turnings are placed in a perforated stainless-steel basket which is immersed in the solution after the leaching, and is allowed to rest there with slow stirring by a stream of air. The reduction is terminated when the Ti^{3+} content reaches about 3 to 5 g/l. In the continuous process the iron is added to the tanks of the leaching system.

The pulp is allowed to settle in continuous rake thickeners. Coagulants, such as joiner's glue, are added to the solution in order to accelerate the settling of fine dispersions. The product from the bottom of the thickener (the slimes) is diluted with cold water and is filtered in drum filters. The dilute solutions obtained are returned to the leaching. The clear solution from the thickeners is forwarded to the crystallization of ferrous sulfate $FeSO_4 \cdot 7H_2O$. To this end, the solution is cooled to 10 to 15°.

The ferrous sulfate crystals have a tendency to adhere strongly to the heat-transfer surfaces (the apparatus walls, which are cooled by water flowing within a jacket, the cooling coil surface), which results in a decrease in the rate of heat removal and reduces the output of the apparatus. Thus, it is most convenient to use continuous vacuum crystallizers in which the precipitate cannot adhere to the walls.

After the crystallization of the $FeSO_4 \cdot 7H_2O$ there is a decrease in the volume of the solution on account of the water of crystallization in the iron sulfate. The resulting solution contains about 140 to 150 g/l TiO_2, 280 to 300 g/l active H_2SO_4, 30 to 35 g/l Fe (as ferrous sulfate), as well as some aluminum, magnesium, and manganese sulfates.

Large amounts of the by-product — ferrous sulfate — may be used in the production of sulfuric acid. For this purpose the ferrous sulfate is ignited to 800 to 900° in the presence of pyrite or coal. The sulfuric anhydride formed is forwarded to the production of sulfuric acid by the contact process. In addition, ferrous sulfate is used to combat plant pests in agriculture.

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Hydrolysis. Metatitanic acid is precipitated from titanium sulfate solutions by hydrolytic decomposition. The main hydrolysis reaction is:

$$TiOSO_4 + H_2O \rightarrow H_2TiO_3 + H_2SO_4.$$

The composition of the solution and the method of hydrolysis used influence strongly the composition and structure of the resulting precipitates. For instance, the production of fine titanium dioxide (used as a pigment) requires that the hydrolysis be carried out in solutions containing 180 to 200 g/l TiO_2 and having an "acid factor" not higher than 2*. From solutions containing up to 120 to 150 g/l TiO_2 metatitanic acid is obtained which upon ignition yields coarse titanium dioxide.

The specifications with regard to the physical properties of titanium dioxide used in metallurgy (for the production of hard alloys, nonferrous metal alloys and titanium metal) are not very strict, and the main requirement is that the product be of the required degree of purity. However, here too (and especially for the production of hard alloys) the product must be of a standard particle size.

Because of its large specific surface, the precipitated metatitanic acid usually contains adsorbed SO_4^{2-} ions which are strongly bound to the precipitate. The sulfate groups are removed completely only by igniting the precipitate to 850 to 900°.

There are two commercial methods for the hydrolysis — the dilution method, and the nucleation method.

The dilution method. The starting solution is concentrated by evaporation to a TiO_2 content of 240 to 260 g/l and an active H_2SO_4 content of 480 to 520 g/l. The concentrated solution is then diluted under strictly controlled conditions, by the addition of water to an active H_2SO_4 content of 380 to 400 g/l. Crystallization nuclei are formed in the solution during dilution, and metatitanic acid then precipitates out.

In order to prevent the premature start of the hydrolysis the evaporation is carried out at 70 to 75° under reduced pressure (60 mm Hg) in vacuum evaporators.

The dilution conditions must be strictly controlled in order to obtain a precipitate with the required structure.

The nucleation method. In order to effect the hydrolysis, nuclei, which are prepared in advance in the form of a colloidal solution of hydrated titanium oxide, are introduced into the titanium sulfate solution. The colloidal solution is obtained by partial neutralization of the titanium sulfate solution with a sodium hydroxide solution (about 100 g/l) to pH = 3. The TiO_2 content of the solution containing the nuclei is about 50 g/l. The nuclei are added in an amount equal to 1% of the TiO_2 content, the solution is stirred, heated to boiling, and allowed to stay at that temperature for 2 to 4 hours. The precipitate contains 95 to 96% of TiO_2.

Metallurgical titanium dioxide is usually produced by the nuclei introduction method, which is less expensive since it permits the use of the sulfate solutions directly after the filtration (without advance concentration by evaporation).

The metatitanic acid precipitate produced by one of the above methods is separated by filtration, and washed on drum or sheet vacuum filters.

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* The "acid factor" is the ratio of the concentration of active H_2SO_4 to the concentration of TiO_2 in the solution (see footnote, p. 180).

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The ignition of metatitanic acid. The ignition of the metatitanic acid precipitate results in the removal of SO_3 and water and in the formation of crystalline titanium dioxide. The water is removed at 200 to 300°, the SO_3 at 500 to 950°.

Depending on the temperature, the ignition yields TiO_2 with the structure of anatase (at temperatures up to 950°) or rutile (above 950°).

In the production of metallurgical titanium dioxide the ignition is carried out at 1000 to 1100°, which ensures complete removal of SO_3. The product is a coarse dioxide with the structure of rutile.

When using the above technique, the materials consumed in the production of one ton of titanium dioxide are:

ilmenite (42 % TiO_2)	3.1 tons
sulfuric acid (as the monohydrate)	4.7 tons
iron turnings	0.24 tons

The sulfuric acid method for the production of titanium dioxide has the disadvantage of being expensive, because of the consumption of large amounts of sulfuric acid to dissolve the iron in the ilmenite (1.76 kg of H_2SO_4 is theoretically needed to dissolve one kg of iron).

Production of titanium dioxide from titanium tetrachloride /11/

The production of titanium dioxide from titanium tetrachloride has recently become of interest. The economic advantages of such a process are evident, as a single process would yield two main products — $TiCl_4$ and TiO_2.

There are three known methods for the production of titanium dioxide from titanium tetrachloride:

1) hydrolysis of aqueous solutions of titanium chloride;

2) decomposition of gaseous titanium chloride by water vapor (gaseous-phase hydrolysis);

3) "combustion" of the chloride in air or oxygen at high temperatures.

Each of these methods is briefly discussed below.

Hydrolysis of aqueous solutions of titanium chloride. In this method aqueous solutions of titanium chloride are prepared in advance. For this purpose, $TiCl_4$ is introduced into cold water or dilute hydrochloric acid. The solution first becomes hot and turbid, which is associated with the hydrolytic precipitation of titanium oxychlorides and hydrated titanium dioxide. However, when further amounts of $TiCl_4$ are bubbled through, the precipitated compound dissolves and clear solutions containing amounts of titanium equivalent to 550 g/l TiO_2 and 600 g/l HCl may be obtained. Evaporation of HCl takes place because of the high temperature of the solution. For this reason the molar ratio Ti : Cl in the solution usually differs from the stoichiometric and varies from 1 to 2.7. The titanium tetrachloride is introduced through a tube immersed in the aqueous solution. In order to prevent clogging of the tube, dry air or an inert gas is passed together with the chloride. The solution is stirred to prevent localized overheating. The concentration of TiO_2 in the starting solutions fluctuates from 150 to 350 g/l.

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The chloride solutions are hydrolyzed by nucleation (seeding) or by the dilution method. The hydrolysis reaction is:

$$TiCl_4 + 3H_2O \rightleftarrows H_2TiO_3 + 4HCl.$$

When using the seeding method for the hydrolysis, the nuclei are precipitated from a part of the solution by neutralization with NaOH to pH 2 to 3 and heating to ~ 80°. The precipitate is then added to the main solution which is heated to 100°. The hydrolysis is rapid and is completed within 10 minutes with the precipitation of 95 to 96% of the titanium from the solution.

The hydrolysis may be successfully carried out without seeding by pouring the concentrated solution of titanium chloride into boiling water and boiling the mixture.

The precipitates formed in the hydrolysis are washed and ignited at 850 to 900° yielding titanium dioxide having the crystal lattice of rutile. High-purity titanium dioxide is obtained by using purified titanium chloride.

Hydrolysis in the gaseous phase. The interaction of water vapor and gaseous $TiCl_4$ at 300 to 400° yields titanium dioxide:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl.$$

The hydrolysis is carried out as a continuous process by feeding a stream of air saturated with water vapor and a stream of air saturated with titanium tetrachloride vapor into a reaction chamber preheated to 300 to 400°. Before entering the chamber each stream is preheated to 300 to 400°. The gases from the hydrolysis chamber are fed to a dust-separation chamber (which is heated to 200 to 400° in order to prevent condensation of the HCl), for the separation of the TiO_2. The TiO_2 may be entrapped in porous ceramic filters. The main difficulty in the process lies in the selection of a material resisting the effect of hydrogen chloride in the presence of water vapor.

Combustion of $TiCl_4$. From the standpoint of chlorine regeneration, the most expedient method for the production of TiO_2 is by the action of oxygen on $TiCl_4$:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2.$$

The reaction takes place at 900 to 1100° and may be carried out as a continuous process.

In one variant of the method, the air stream and the $TiCl_4$ vapors (which are usually diluted with nitrogen) are preheated to 1000 to 1100° and fed to reaction chambers in which the temperature is maintained at 750°. The titanium tetrachloride reacts with the air at the exit of the gas-feeding tubes, with the formation of a yellow-green flame. The gas stream entrains the titanium dioxide particles (as smoke) to the dust-separation chamber. The amounts of gas introduced per liter of reaction-chamber volume are: 0.5 l $TiCl_4$, 0.5 l nitrogen, and 1 l air. The selection of [structural] materials for the above process is easier than in the case of gaseous-phase hydrolysis.

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46. PRODUCTION OF METALLIC TITANIUM

The high chemical activity of titanium makes the production of the pure metal from its compounds difficult. At the same time, the modern specifications for titanium require a high-purity metal.

As mentioned above, oxygen, nitrogen, and carbon present as impurities increase the strength of titanium and reduce its ductility. The presence of hydrogen has little effect on the hardness and strength of titanium, but causes a sharp decrease in impact strength. This is attributed to the precipitation of titanium hydrides on the grain boundaries.

TABLE 34

Free energy changes in the interaction of titanium with various gases

Reaction	ΔF, kcal	
	25° C	800° C
$Ti + O_2 = TiO_2$	—212	—186.5
$2Ti + CO_2 = TiO_2 + TiC$	—175	—152
$Ti + \frac{1}{2} N_2 = TiN$	—73.4	—69
$3Ti + 2CO = TiO_2 + 2TiC$	—258.2	—217
$Ti + 2H_2O = TiO_2 + 2H_2$	—51.5	—48.2
$Ti + 2CO_2 = TiO_2 + 2CO$	—44.7	—48.2
$Ti + C = TiC$	—57.2	—60

The reactions of titanium with oxygen, nitrogen, carbon, carbon oxides, and water vapor are accompanied by a large decrease in free energy (see Table 34). Hence, very small amounts of the gases mentioned above and carbon react with the titanium yielding titanium oxides, carbide, and nitride. The tendency of titanium to dissolve oxygen and nitrogen must be allowed for.

The above data show that at any stage of the production of titanium measures must be taken to prevent it from reacting with oxygen, nitrogen, water vapor, carbon, and carbon-containing gases. This is accomplished by conducting the reduction and melting of the metals in hermetically sealed equipment under an inert-gas atmosphere (argon, helium) or in vacuo. One of the important conditions is that the starting titanium compounds and the reducing agents used be of a high purity.

The production methods of metallic titanium may be divided as follows:

1) reduction of titanium tetrachloride by magnesium or sodium;
2) reduction of titanium dioxide by calcium or calcium hydride;
3) electrolytic methods;
4) thermal dissociation of titanium halides.

The largest part of the titanium produced today is made by reduction of titanium chloride with magnesium or sodium. A flow sheet of these processes is shown in Figure 97 and Figure 103.

Of the two reducing agents used, magnesium was the first to be used in the development of industrial titanium production. It was assumed that the reduction of $TiCl_4$ with sodium would be more difficult to accomplish, as sodium and $TiCl_4$ react with the evolution of large amounts

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of heat, and the reaction is explosive and difficult to control. Moreover, the high chemical activity of sodium necessitates special preventive measures when dealing with it. Investigations have shown, however, that the difficulties accompanying the reduction of titanium chloride by sodium have been exaggerated to a great extent. Also, thermal reduction with sodium has some advantages over the thermal reduction with magnesium (see below, Section 48).

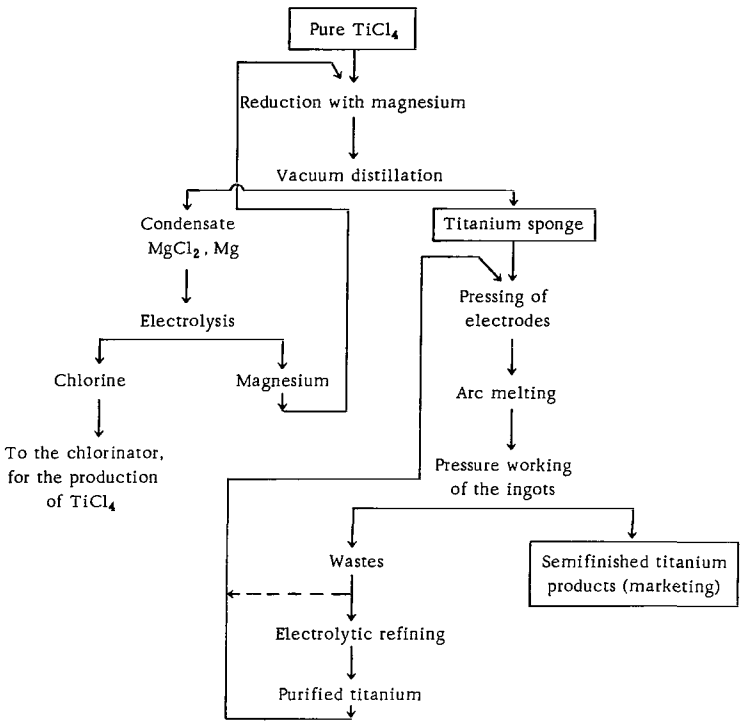

FIGURE 97. Flow sheet of commercial methods for the production of titanium from titanium tetrachloride.

Depending on the reduction method employed, titanium is obtained either as a spongy material or as a powder. Subsequently, it is converted into the solid metal (after separation of the slag and the excess reducing agent) by fusion or occasionally by powder metallurgy methods.

47. REDUCTION OF TITANIUM TETRACHLORIDE WITH MAGNESIUM (THE KROLL PROCESS)

Physicochemical principles of the process

The reduction of titanium chloride with magnesium is carried out in hermetically sealed steel reactors filled with an inert gas (argon or

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helium). A pool of molten magnesium lies at the bottom of the reactor, and titanium tetrachloride is fed to the apparatus (from a pressure tank) at a controlled rate; the $TiCl_4$ vapor reacts with the magnesium as follows:

$$TiCl_4 \text{ (gas)} + 2Mg \text{ (liquid)} \rightarrow Ti \text{ (solid)} + 2MgCl_2 \text{ (liquid)}.$$

The reaction is exothermic. The heat evolved (122 kcal per mole of $TiCl_4$ or 2545 kcal per kilo of titanium) suffices to maintain the reaction without a supply of heat from the outside.

It would seem at first sight that the reduction with magnesium should proceed without difficulties up to the quantitative utilization of the magnesium, since at the process temperature (800 to 900°) the phases should be separated into layers: the upper layer consisting of liquid magnesium (density 1.47 g/cm^3), the lower of $MgCl_2$ (density 1.67 g/cm^3), and on the bottom heavier particles consisting of titanium sponge agglomerates (density 4.5 g/cm^3). Thus, the liquid magnesium upper layer should be accessible for reaction with the $TiCl_4$ vapors throughout the reduction process.

The true mechanism of the reduction is more complex and has not been adequately studied. Since this is a batch process, its rate varies with the amount of titanium chloride added into the reactor and consequently, with the amount of magnesium consumed and the accumulated reaction products — titanium sponge and magnesium chloride (slag).

At the start, when less than 60% of the $TiCl_4$ have been introduced into the apparatus, the reduction takes place very rapidly. After about 50% of the magnesium have been consumed the remaining magnesium disappears as a one-phase melt, since it is completely absorbed in the pores of the sponge; this leads to a decrease in the reduction rate. The accumulating slag (liquid magnesium chloride) also reduces the process rate. One liter of magnesium yields 0.354 l of titanium and 3.68 l of magnesium chloride. The level of the magnesium chloride gradually rises, above the sponge level, when the reaction practically ceases. This is shown by a decrease in the temperature and an increase in the pressure in the reactor (since the titanium tetrachloride supplied to the reactor is not consumed).

Magnesium chloride is discharged periodically to bare the surface of the sponge and to utilize more fully the working volume of the reactor. This results in an increase in the reaction rate.

Rather than charging the apparatus with the whole amount of magnesium at the start, it is better to add the magnesium periodically in order to have a uniform-rate process. The periodic addition of magnesium results in a higher degree of utilization of the magnesium and in the production of titanium sponge of more uniform composition.

The lower temperature limit of the reduction is the melting point of $MgCl_2$ (714°) while the upper limit is 975°. Above that temperature the titanium is fused together with the iron (the melting point of the titanium-iron eutectic is 1085°). Moreover, the iron reacts with the $TiCl_4$ yielding lower titanium chlorides and iron titanide (FeTi):

$$Fe + 2FiCl_4 = FeCl_2 + 2TiCl_3;$$
$$Fe + TiCl_4 = FeCl_2 + TiCl_2;$$
$$3Ti + 2FeCl_2 = 2FeTi + TiCl_4;$$

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$$Fe + 2TiCl_2 = FeTi + TiCl_4;$$
$$Fe + 4TiCl_3 = FeTi + 3TiCl_4.$$

This may result in the contamination of titanium with iron, and to a rapid failure of the equipment. The temperature range in which the reduction may be carried out is fairly wide (720 to 975°). In practice the process is carried out at 800 to 900°.

The temperature may be maintained by controlling the rate of supply of titanium tetrachloride. In order to increase the output of the apparatus, a part of the excess heat is removed by cooling the outer walls of the reactor with cold air.

Lower titanium chlorides are formed towards the end of the reduction when most of the magnesium has been consumed; some of the reactions involved are:

$$2TiCl_4 + Mg = 2TiCl_3 + MgCl_2;$$
$$TiCl_4 + Mg = TiCl_2 + MgCl_2;$$
$$3TiCl_4 + Ti = 4TiCl_3;$$
$$TiCl_4 + Ti = 2TiCl_2.$$

The lower titanium chlorides dissolve in the liquid magnesium chloride. As the melt flows through the pores of the sponge, the lower chlorides are partly reduced by the magnesium in the pores.

An excess of magnesium (about 15 to 25% of the theoretical amount needed) is used in order to ensure quantitative reduction, and at the end of the reduction (i. e., after the interruption of the supply of $TiCl_4$) the reactor is held at a high temperature (900 to 920°) to complete the reduction of the lower chlorides.

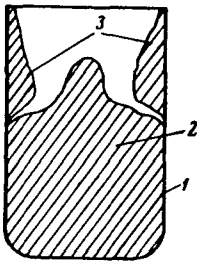

FIGURE 98. Approximate disposition of the titanium sponge (the reaction mass) towards the end of the reduction.

1 — reaction vessel; 2 — sponge ("bloom"); 3 — sponge lining.

The mechanism of formation of the sponge in the apparatus has not yet been finally clarified. Investigations with industrial equipment have shown that the main factor governing the reduction process is the rate of supply of $TiCl_4$. This factor governs the growth and structure of the titanium sponge, and the temperature and pressure inside the equipment. It has been established that the reduction of the tetrachloride by magnesium is autocatalytic*. The reaction rate increases with the formation and the growth of the titanium sponge. In other words, the reaction rate depends on the development of the surface of the titanium sponge formed in the reaction. This is governed mainly by the rate of supply of $TiCl_4$ to the apparatus /26/.

Figure 98 shows the approximate disposition of the titanium sponge in an industrial vessel operating without periodical addition of magnesium. The bulk of the sponge filling the apparatus (about 75 to 80% of it) is the so-called bloom.

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* Autocatalytic reactions proceed at a gradually increasing rate because of the catalytic effect of the reaction products.

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Of the total amount of magnesium chloride formed, 75 to 85% is drained during the reduction and forwarded to electrolysis.

Types of reactors used for thermal reduction with magnesium /8/

In titanium plants the reduction of titanium tetrachloride by magnesium is carried out in steel reactors designed to produce from 500 to 600 to 1000 to 1500 kg of titanium sponge in one operation. Most of the body of the equipment (retort) is made of stainless steel (18% Cr, 8% Ni, 2% Mo) which resists oxidation and has a satisfactory strength at 950 to 1000°. Reactors made of such steel may be withdrawn from the furnace at 700 to 800° and directly cooled with water, with consequent increase in the turnover.

The retort is covered with a lid, which is fastened to the flange with bolts*. Hermetic sealing is accomplished with the aid of rubber-ring gaskets cooled by water flowing through a jacket. Sleeves in the lid serve to introduce solid or liquid magnesium, to feed titanium tetrachloride from the pressure tank, to join the installation to the vacuum system, and for the supply of argon.

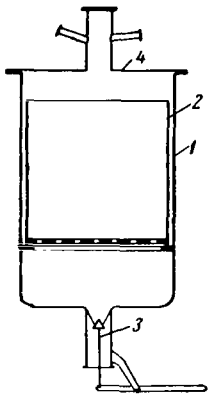

FIGURE 99. Diagram of an insert pot reactor with a perforated bottom.

1—body; 2—insert pot with perforated bottom; 3—device for discharging slag; 4—lid with sleeves for the introduction of magnesium, chloride, and protective gas.

Two types of reactors are used: reactors with an insert pot, and without an insert pot. The main difference between various types of reactors with an insert pot is the accessory serving to discharge magnesium chloride.

The simplest technique of slag evacuation is employed in reactors with an insert pot with a perforated bottom (Figure 99). At the beginning of the process the liquid magnesium level is slightly above the perforated bottom of the pot. The titanium sponge gradually grows and fills the pot. The liquid magnesium is absorbed into the sponge pores from below. Magnesium chloride flows through the perforations into the retort space below the pot, and is discharged.

Reactors with an insert pot have the following disadvantages: a low coefficient of utilization of the working volume of the retort (0.4 to 0.45); a ring-shaped gap between the pot and the retort which interferes with heat transfer and reduces the rate of the process; the complex design of slag discharge mechanism. As a result extensive use is made of reactors without an insert pot, in which the reaction products (the reaction mass) accumulates inside the retort. In these reactors the slag is discharged by a simple technique (through a sleeve fitted to the bottom of the retort); the volume of the

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* The lid is occasionally welded to the flange of the retort. At the end of the operation the welded joint is cut on a lathe and the lid is removed.

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retort is utilized more fully (the utilization coefficient is 0.5 to 0.6); the heat is led off more efficiently through the retort walls which are cooled by a stream of air, so that the process rate can be increased. The temperature in reactors of this type may be controlled by simply taking the temperature of the exterior of the walls at several height levels of the retort, without the need for inserting thermocouples into the reactor.

The reactors are heated in electrical or gas-fired furnaces. It must, however, be borne in mind that heating is required only at the beginning of the reaction (heating the installation fusion of the first batch of magnesium charged) and at its end.

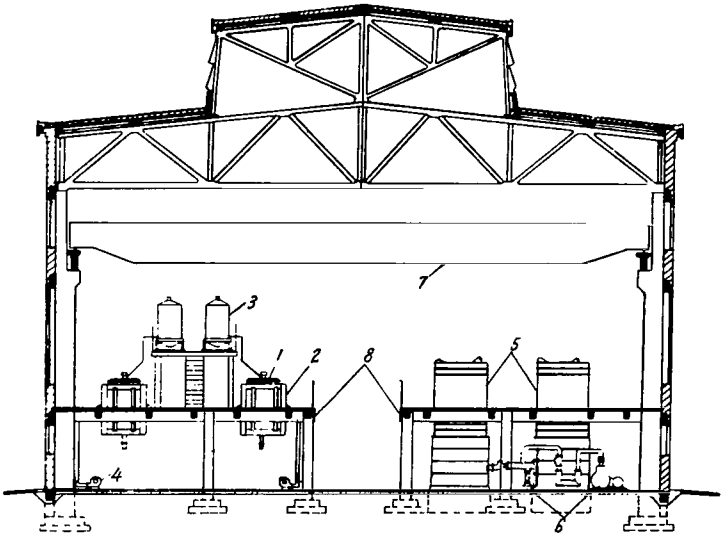

FIGURE 100. Installation used for industrial-scale reduction of $TiCl_4$ by magnesium.

1 — reactors; 2 — furnace; 3 — pressure vessel with $TiCl_4$; 4 — fan; 5 — distillation unit; 6 — vacuum pumps; 7 — overhead hoist; 8 — platform.

Figure 100 shows one of the setups used for the large-scale reduction.

The reduction process — conditions and control

The process conditions depend on the type of apparatus used, its size, the manner in which magnesium is introduced (liquid or a solid, with or without periodical replenishment) and the rate of removal of heat from the walls. As an example, the reduction process in an apparatus without an insert pot and without replenishment of magnesium is described below.

The installation is assembled and checked in a special room. The lid is fitted to the retort and the tightness checked. For this purpose, the air is evacuated and the leak rate measured (by measuring the increase in pressure). The assembled installation is inserted into the furnace with

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the aid of a hoist, and filled with argon (or helium). The apparatus is heated to 700 to 750° and is charged with liquid magnesium*; compressed $TiCl_4$ is then supplied from a tank. The furnace is disconnected and the temperature maintained at 850 to 900° by controlling the rate of supply of titanium chloride.

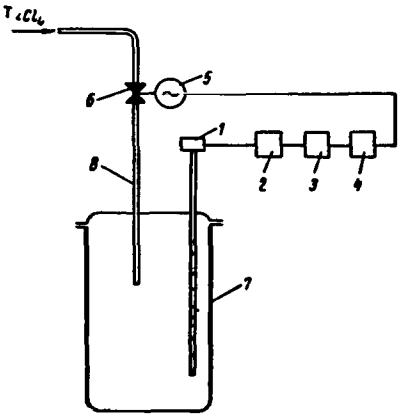

FIGURE 101. Diagram of the automatic control of reduction of $TiCl_4$ with magnesium.

1 — multiple-junction thermocouple; 2 — maximum-temperature selector; 3 — measuring device (electronic potentiometer); 4 — isodromic [sic] regulator controlling the actuating mechanism; 5 — actuating mechanism connected to the $TiCl_4$-supply valve; 6 — valve; 7 — body of the apparatus; 8 — tube for the supply of $TiCl_4$.

In order to increase the output of the installation, part of the excess heat is removed by cooling the retort with air, which is blown in the circular gap between the furnace and the retort.

The slag is discharged for the first time after about 60% of the magnesium has been consumed. The argon pressure in the apparatus is increased somewhat during the discharge. Subsequently the slag is discharged after about 80% and 95% of the $TiCl_4$ have been consumed.

After the whole amount of the titanium chloride has been introduced into the reactor, the slag is discharged for the last time and the reactor is held for 30 to 60 minutes, at 900 to 920°, in order to reduce the lower chlorides. The furnace is then shut off and when the temperature reaches 600 to 700° the reactor is withdrawn from the furnace and placed in a special nest in which water-cooling takes place. The cooled installation is then dismantled.

During the reduction process the required temperature is maintained automatically in the reactor by controlling the rate of supply of the $TiCl_4$. The automatic control of the temperature is complicated by the fact that the temperature field of the reactor is nonuniform.

As the reaction proceeds the maximum temperature shifts upwards, together with the reaction zone. The retort walls are at their highest temperature within the ring-shaped region in which the reaction takes place at the most rapid rate at the given moment. Hence, the temperature is measured with several thermocouples fitted at different height levels in the retort. As the reaction zone shifts, a special device ("the maximum-temperature selector") automatically connects the $TiCl_4$-supply regulator to the thermocouple which is measuring the highest temperature at that instant. A diagram of the temperature control system is shown in Figure 101 /8/.

The above scheme does not ensure the maximum process rate or the maintenance of standard working conditions. This is because the determining effect of the rate of supply of $TiCl_4$ on the process rate is not taken into account.

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* When using solid magnesium as feed, the magnesium bars are first etched in hydrochloric acid, then rinsed, dried, and charged into the apparatus before the assembly.

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As a result, a new automatic control system has been recently developed; it consists in the optimum programming of the supply of $TiCl_4$ to the installation. The temperature and pressure are used only as check, but they do not determine the rate of supply of $TiCl_4$ to the installation. The reduction time becomes shorter and enables the process to be carried out under standard conditions /26/

Processing of the reduction product

The reduction product (the reaction mass) contains 55 to 65% titanium, 20 to 30% residual $MgCl_2$, and 10 to 20% excess magnesium.

There are two known methods for the purification of titanium sponge — leaching and vacuum distillation.

The leaching method was used in the first titanium-producing plants. The reaction mass (which was drilled out of the retort or the insert pot) was treated with dilute (about 1%) cold hydrochloric acid, with the purpose of removing the bulk of magnesium and magnesium chloride. The sponge is then subjected to wet milling in a ball mill, and is leached with 10% hydrochloric acid at 45° with the purpose of removing the residual magnesium and magnesium chloride. The powder is then rinsed with water, dried, and passed through an electromagnetic separator to remove iron particles which may have contaminated the sponge during the drilling.

The titanium powder produced contains 0.1 to 0.3% hydrogen (which is evolved when magnesium is dissolved in the acid) and up to 0.1% oxygen, whose presence is caused by the oxidation of titanium during the wet processing. The oxidation is more rapid if heat is applied during the dissolution of magnesium in the acid. The hydrogen is removed (and its concentration reduced to a permissible level) during arc melting in vacuum, but the oxygen remains and the metal has an increased hardness.

A method employing vacuum distillation to remove magnesium and magnesium chloride from the reaction mixture, developed with the purpose of improving the quality of the metal, has now superseded the leaching method.

The vacuum distillation method. The purification of the sponge by this method utilizes the relatively high vapor pressure of magnesium and magnesium chloride at 850 to 950°, and the very low vapor pressure of titanium at that temperature:

Temperature, °C	700	800	900	1000
Vapor pressure, mm Hg:				
of magnesium	5	25	80	250
of magnesium chloride	—	2.2	8.0	80

Prolonged heating of titanium sponge in high vacuum ($2 \cdot 10^{-3} - 3 \cdot 10^{-4}$ mm Hg) in steel retorts, at 900 to 925°, causes vaporization of magnesium and magnesium chloride, which condense on the surface of a water-cooled condenser. The condensate is electrolyzed in order to recover the magnesium.

In industrial practice the distillation is carried out by one of two methods:

1) in the retort (or insert pot) which was used for the reduction, without removing the reaction mixture.

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2) the reaction mixture is extracted from the retort (or the insert pot) with the aid of a pneumatic chisel or by drilling on a lathe and is charged in a granulated form into a perforated steel basket which is fitted into the distillation retort.

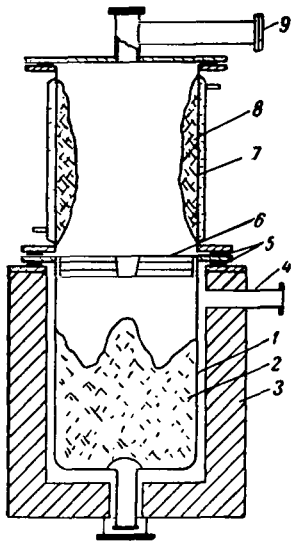

FIGURE 102. Thermal purification of titanium sponge in vacuo, without transfer from the reduction vessel.

1—reduction vessel (retort); 2—titanium sponge; 3—electrical furnace with a sealed jacket; 4—sleeve connection to vacuum system (to produce countervacuum in the furnace); 5—rubber gaskets; 6—screens; 7—water-cooled condenser; 8—condensate—Mg and $MgCl_2$; 9—sleeve connection to the vacuum system.

The second method permits an increase in the output of the distillation unit, because of the more complete filling of the retort. However, the removal of the reaction mass and its transfer to the basket is accompanied by the absorption of moisture (by magnesium chloride), and formation of the nonvolatile hydroxychloride MgOHCl, which results in an increase in the oxygen content of the sponge. For this reason it is recommended that the removal and charging of the mass be carried out in special dry rooms, with an atmospheric moisture content not higher than 0.5% (dew point -40°). The need for dry rooms increases the capital investment. Moreover, the working conditions in such rooms are unfavorable to the health of the presonnel.

In order to prevent the retort walls (which are heated to 900 to 1000°) from caving in under the effect of the atmospheric pressure, the furnace jacket is hermetically sealed and a "countervacuum" of about 0.2 mm Hg is maintained in it. A vacuum of the order of 10^{-4} mm Hg is created inside the retort with the aid of a vacuum system consisting of a rotary and a diffusion pump (see Figure 83).

A water-cooled condenser is fitted to the flange of the retort if the distillation is carried out in the retort used for the reduction, without transferring the reaction mixture /33/. The retort is then transferred to the distillation furnace (Figure 102). The retort is allowed to remain in the furnace for a prolonged time (20 to 25 hours) at 900 to 925°, and is then withdrawn, cooled, transferred to a special room, dismantled, and the sponge is excavated with pneumatic chisels.

Depending on the degree of adhesion of the bulk of the titanium sponge (the bloom) it is withdrawn either in one piece or in a granulated form. The fraction of the sponge removed from the walls is collected separately since it contains larger amounts of impurities. The sponge particles are crushed to the required particle size first with a hammer or in a press, and then in a mill.

The refined sponge is characterized by the following approximate impurity contents: 0.0016% H_2, 0.05% O_2, 0.002% N_2, 0.07% Cl, 0.08% Mg, 0.13% Fe, 0.03% Si, 0.1% C.

After fusion in an arc furnace, the hardness of the titanium is 100 to 150 kg/mm^2.

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The condensate produced contains magnesium and magnesium chloride, and is returned to the magnesium production plant.

The vacuum distillation method has the disadvantages of low output, high consumption of electrical energy (18 to 22 kwh/kg sponge), and the need for a complex equipment to create the high vacuum.

The technical and economical indexes of the process

A well-designed titanium plant must include electrolysis of magnesium chloride, in order to produce magnesium and chlorine as by-products from the recycled material (see Figure 97).

When using titanium slags containing 80 to 85% TiO_2 as the starting raw material, the total degree of extraction of titanium from the slags and the sponge is about 72% (without taking into account the recovery of titanium from the wastes).

The approximate degrees of extraction of titanium in the separate stages are, in% :

From slags into pellets	97—98
From pellets into technical chloride	85—86
From technical into purified chloride	~95
From purified chloride into commercial Ti sponge	90—91

The degree of extraction may be increased by reducing the amount of rejected sponge and by its processing (e. g., by electrolytic refining), by improving the chlorination and chloride-purification processes, by recovering the titanium from the chlorination and purification wastes, and by reducing the mechanical losses in the pelletizing stage.

In the total cost of titanium sponge, about 76.2% are accounted for by the cost of titanium tetrachloride and magnesium. The power consumption accounts for 2.4%, wages for 5.5%, and overheads for 15.6% of the cost. This shows that the cost of the sponge may be reduced mainly by reducing the price of titanium tetrachloride.

48. REDUCTION OF TITANIUM TETRACHLORIDE BY SODIUM /9/

As mentioned above, many plants use sodium as the reducing agent. There are several advantages of sodium over magnesium.

1. Sodium has a lower melting point (98°), which facilitates its piping and feeding into the reactor. Oxide films and certain impurities are readily removed from sodium by filtration.

2. The reduction of $TiCl_4$ by sodium is more rapid, and the sodium utilization coefficient is as high as 100% (in the reduction with magnesium it ranges between 70 and 90%). The quantitative utilization of the reducing agents permits the process to be carried out without tapping off the sodium chloride, which simplifies the construction and maintenance of the equipment.

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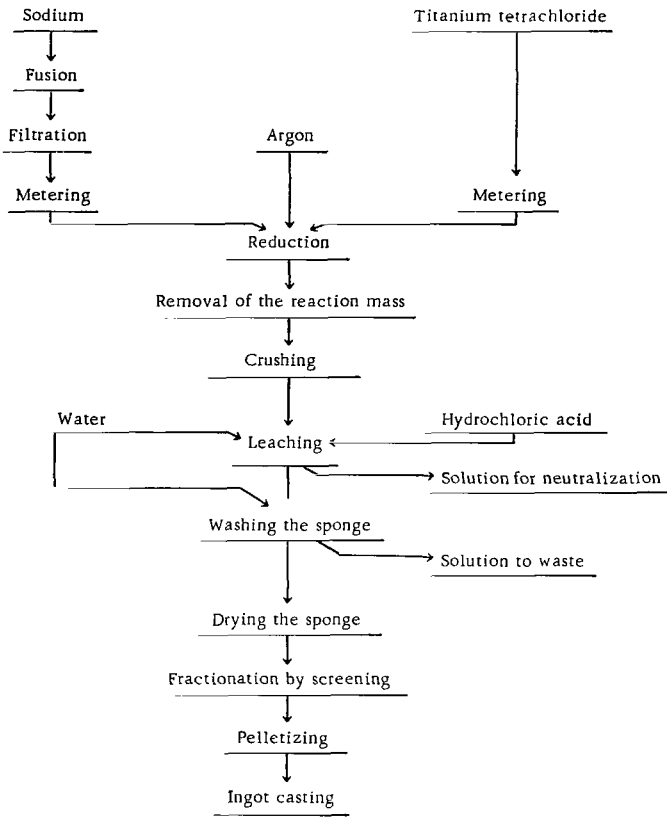

FIGURE 103. Flow sheet of the production of titanium by thermal reduction with sodium.

3. Unlike magnesium chloride, sodium chloride is only slightly hygroscopic and does not hydrolyze in aqueous solutions. This, as well as the negligible concentration of elemental sodium in the reaction mixture, makes it possible to separate slag from titanium by simply leaching with water, thus avoiding vacuum distillation, which is a complex and energy-consuming process.

4. Titanium powder produced by reduction is easier to use than titanium sponge for the production of alloys since it is readily mixed with the alloying additives. This results in the formation of uniform alloys.

Some of the disadvantages of the method are: the volume of the reducing vessel and slag per kg of titanium are larger than when magnesium is used, which requires the use of large sized equipment; the reduction is accompanied by the evolution of large quantities of heat (about 70% more than when magnesium is used), which causes difficulties in the removal of the heat; the safety precautions required are more stringent than in the case of magnesium, because of the high chemical reactivity of sodium.

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However, it was found in practice that these disadvantages and difficulties can be overcome.

The overall flow sheet of thermal reduction with sodium is shown in Figure 103.

Reduction

The reduction of $TiCl_4$ by sodium may be carried out in three temperature ranges: at temperatures below the melting point of sodium chloride (i. e., below 801°); at 801 to 883°, i. e., between the melting point of sodium chloride and the boiling point of sodium; and at temperatures above the boiling point of sodium. In industrial practice the reduction is carried out in the range 801 to 883°. In this case the reaction occurs mainly between gaseous $TiCl_4$ and liquid sodium:

$$TiCl_4\,(gas) + 4Na\,(liquid) = Ti\,(solid) + 4NaCl\,(liquid) + 172.8\ kcal.$$

However, a noticeable part of the reaction takes place in the gaseous phase above the melt since at 801° the vapor pressure of sodium is about 340 mm Hg:

$$TiCl_4\,(gas) + 4Na\,(gas) = Ti\,(solid) + 4NaCl\,(liquid) + 262.0\ kcal.$$

The thermal effect of the reduction by sodium vapor is 84 kcal higher than in the reduction by liquid sodium.

The above equations represent the overall reactions. In fact, the reduction takes place through stages involving the formation of lower titanium chlorides, $TiCl_3$ and $TiCl_2$, which dissolve in sodium chloride*.

The lower chlorides are formed through the interaction of gaseous $TiCl_4$ with titanium particles:

$$3TiCl_4\,(gas) + Ti\,(solid) \rightleftarrows 4TiCl_3\,(liquid),$$
$$TiCl_4\,(gas) + Ti\,(solid) \rightleftarrows 2TiCl_2\,(liquid).$$

The lower chlorides then diffuse into the bulk of the melt. Here they may undergo disproportionation by the reactions written above (which in this case proceed from right to left) yielding finely-dispersed titanium powder.

The following reactions are also possible:

$$2TiCl_3\,(liquid) \rightleftarrows TiCl_2\,(liquid) + TiCl_4\,(gas);$$
$$3TiCl_2\,(liquid) \rightleftarrows 2TiCl_3\,(liquid) + Ti\,(solid).$$

Sodium chloride and $TiCl_2$ form a eutectic mixture (at a $TiCl_2$ concentration of 33% by weight, which corresponds to the composition $2NaCl + TiCl_2$) with a melting point of 605°. In the system $TiCl_3$ — NaCl there is a eutectic mixture with the composition of 43% by weight $TiCl_3$ and 57% by weight NaCl, which melts at 554°. In addition, there is a chemical compound with the composition $TiCl_3 \cdot 3NaCl$. A ternary compound having the composition $13\,NaCl \cdot 3TiCl_3 \cdot 2TiCl_2$ may be formed in the presence of both chlorides. Sodium is dissolved by molten NaCl, as shown by the data below:

Temperature, °C	810	825	890	930	950
Solubility of sodium, %	1.12	1.99	3.88	9.63	11.02

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* The properties of the lower chlorides have been described on p. 161.

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The reduction is carried out in stainless-steel reactors, into which measured amounts of $TiCl_4$ and liquid Na are charged simultaneously at a ratio close to the stoichiometric (i. e., 2.06 kg $TiCl_4$ per kg Na).

The apparatus is first evacuated, then filled with argon and heated in a furnace to about 650 to 700°. The reaction is allowed to proceed for a certain time, during which a liquid melt accumulates in the retort; the furnace is then shut off and the process continues at the expense of the heat of reaction, which maintains the temperature at 850 to 880°. The excess heat is removed by blowing air round the retort.

In the first stage of the reaction, the reduction takes place to a considerable extent in the gaseous phase, with the formation of finely-dispersed titanium and the lower chlorides. The lower chlorides dissolve in the sodium chloride, and are reduced by the sodium present in the melt, yielding titanium crystals which are heavier and thus settle to the bottom. At the end of the process the furnace is turned on and the retort is maintained at 950 to 970° in order to effect quantitative reduction of the lower chlorides and to cause consolidation of the metal particles.

In one plant in the USA (in the city of Ashtabula) the process is carried out in reactors made of two steel layers (the inner layer is high-carbon steel, the outer is stainless steel). The retort has a diameter of 1.5 m, a height of 4.2 m, and a wall thickness of 25 mm. Electrolytic sodium is used as the reducing agent. It is supplied in metallic drums, under a protective layer of paraffin, or in tank cars in an argon atmosphere. In order to pump the sodium out of the tank car it is melted with the aid of oil (heated to 120°) circulating within a coil fitted in the tank car. The sodium is purified by filtration through 20 layers of a 0.044 mm nickel gauze and a porous metallic filter with 20 μ holes. The purified sodium contains not more than 0.05% impurities. The sodium and titanium chlorides are continuously metered into the reactor for 5 to 7 hours. In order to complete the reaction the furnace is turned on and the reactor is allowed to remain at about 1000° for 4 to 6 hours, the reactor is then cooled for 2 to 4 hours and transferred to a "nest" in which it is cooled by a forced flow of air.

The rate of supply of $TiCl_4$ to the reactor is on the average 400 kg/m^2. hr, which is twice that used in the thermal reduction by magnesium. Each reduction cycle yields about one ton of titanium.

Processing of the reaction mixture

The reaction mixture containing 17% Ti, 83% NaCl and very small amounts of impurities (sodium and the lower chlorides) is taken out of the retort by cutting with a special drill and is then passed through a screen with 10 mm holes. The coarse fraction is crushed in a hammer mill. The crushed material is leached with water containing up to 1% HCl in rubber-lined steel vats fitted with stirrers. The material is slowly added and the hydrogen evolved in the reaction between the sodium and the water is driven off with the aid of an exhaust system.

The mixture is stirred for about 30 minutes and the titanium powder is separated from the solution by centrifuging. The powder is then dried in a vacuum drier under a pressure of 50 mm Hg.

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Titanium powders have a particle size ranging from +2.4 to -0.07 mm. The bulk of the particles have a size between 2.4 and 0.2 mm. The approximate concentration of impurities is: 0.01 to 0.7% C, 0.04 to 0.15% O, 0.001 to 0.02% N, and 0.005 to 0.019 H.

The titanium is cast into ingots with a Brinell hardness of 110 to 160 kg/mm^2 in an arc furnace. Its mechanical properties are not inferior to the titanium produced by thermal reduction with magnesium.

Two-stage thermal reduction with sodium

An improved version of the reduction of titanium chloride by sodium is the recently developed two-stage reduction process. In the first stage the reduction is carried out intil a eutectic melt whose composition corresponds to 2NaCl + $TiCl_2$ is formed. In the second stage the dichloride is reduced to titanium by the sodium present in the melt:

First stage

$$TiCl_4(gas) + 2Na(liquid) = 2NaCl(liquid) + TiCl_2(liquid) + 111.3 \text{ kcal.}$$

Second stage

$$2NaCl(liquid) + TiCl_2(liquid) + 2Na(liquid) = 4NaCl(liquid) + Ti(solid) + 63.5 \text{ kcal.}$$

Of the total amount of heat, 64% is evolved in the first and 36% in the second stage. This results in a noticeable alleviation of the problem of heat removal from the reactor. The second important advantage of the two-stage process is that favorable conditions are created for the growth of large titanium crystals in the second stage, in which the reduction takes place in the melt. The large-sized crystalline dendrites formed (50 mm or larger) are distinguished by their high purity.

The two-stage reduction can easily be carried out as a semicontinuous process. In the first stage sodium and titanium chloride are simultaneously charged into the steel reactor, at a molar ratio of 2 : 1. The reduction is carried out at 700 to 750° in an argon atmosphere. After the accumulation of a liquid melt (of the composition 2NaCl + $TiCl_2$) in the apparatus, the melt is conveyed by argon pressure through a heated steel tube into the second-stage reactor. The reduction is completed in the second reactor, at temperatures between 650 and 900°. The temperature is controlled by varying the rate of supply of liquid sodium to the reactor. At the end of the reaction the reactor is held at 950° and is then cooled. The withdrawal of the cake and its leaching are carried out in the same manner as that described above for the one-stage process.

Casting the coarsely crystalline titanium yielded ingots with a Brinell hardness of 85.5 kg/mm^2, a tensile strength of 25 kg/mm^2, and an elongation of 56%; these values are close to the values obtained with extremely pure (iodide) titanium.

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49. REDUCTION OF TITANIUM DIOXIDE

Titanium is also produced by the reduction of titanium dioxide. When selecting a reducing agent for titanium dioxide, consideration must be given to the fact that the reduction proceeds through an intermediate stage involving the formation of titanium monoxide TiO, which is a very stable chemical compound.

TABLE 35

Free energy of formation of some metallic oxides

Oxide	ΔF, kcal/g-atom O	
	25°C	1000°C
CaO	-146	-121
MgO	-137.2	-112
$\frac{1}{3}$ Al_2O_3	-125	-100
TiO	-116	- 88.0
Na_2O	- 89.2	- 55.7

Of the available reducing agents, calcium has the highest affinity for oxygen and is able to reduce titanium dioxide to the metal (Table 35). However, even the use of so strong a reducing agent does not yield titanium with an oxygen content below 0.2%. This is due to the solubility of oxygen in titanium (12.5% by weight of 30 at.%), and the fact that the bond between oxygen and titanium is strengthened as the oxygen concentration in the solid solution is reduced.

The free energy of formation of solid solutions of oxygen in titanium at 1000° is listed below:

Oxygen concentration, at.%	0.2	1.6	10	20	30
ΔF, kcal/g-atom O	-122.0	-112.5	-108.7	-100.2	-92.5

In a solid solution containing 0.2 at.% (or 0.07% by weight) of oxygen, the affinity of oxygen for titanium is equal to the affinity of oxygen for calcium at 1000° (see above). Under these conditions, quantitative removal of oxygen is impossible.

Calcium hydride is also used as a reducing agent for TiO_2.

As a reducing agent, magnesium is inferior to calcium. When TiO_2 is reduced with magnesium the reaction proceeds preferentially until the lower oxide TiO or solid solutions of oxygen in titanium are formed.

Reduction by calcium

The reduction involves the following exothermic reaction:

$$TiO_2 + 2Ca = Ti + 2CaO + 85.4 \text{ kcal.}$$

The heat evolved (about 530 kcal per kg of stoichiometric mixture) is not sufficient to maintain a spontaneous reaction, and external heating is necessary.

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The reduction is carried out in argon atmosphere at 1000 to 1100°. At that temperature the calcium is liquid, and a fraction of it is in the gaseous stage (the vapor pressure of calcium at 1000° is 11 mm Hg), which ensures good contact between the calcium and the titanium dioxide. The calcium used in the reduction must be preliminarily purified by distillation and free from nitrogen and carbon (in order to prevent contamination of titanium by these elements).

The reduction yields fine grained titanium (particle size 2 to 3 μ) since the presence of strata of refractory calcium oxide interferes with the growth of titanium particles. The growth of the particles is favored by the addition of $CaCl_2$ (about one mole of $CaCl_2$ per 2 moles of CaO), which forms a liquid phase.

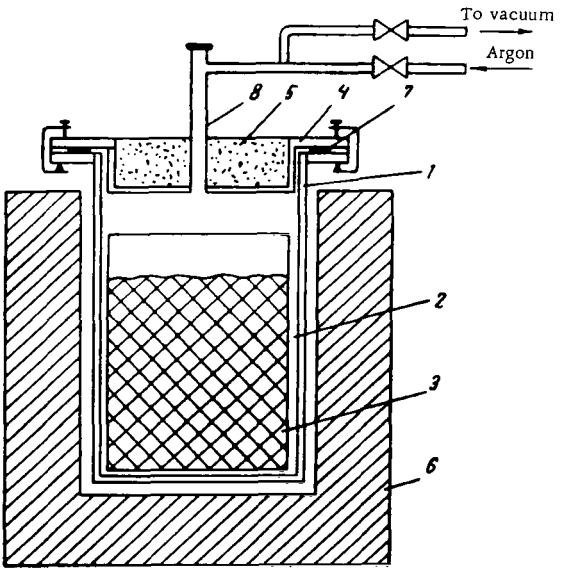

FIGURE 104. Reactor for the reduction of titanium dioxide with calcium.
1—body (retort); 2—steel crucible; 3—pelletized charge; 4—lid; 5—thermal insulation packing; 6—electrical furnace; 7—seals; 8—sleeve connections to the pump or the argon source.

The reduction is carried out in hermetically sealed reactors made of refractory steel, which are charged with a pelletized mixture of titanium dioxide, calcium chloride, and calcium (Figure 104). The calcium used is in the form of fine particles or turnings. The reactor is evacuated, then filled with argon, heated to 1000 to 1100° and held at that temperature for about one hour.

In order to prevent partial removal of calcium from the reaction zone by condensation on the colder reactor lid, the reactor is placed in a furnace in which a uniform temperature is maintained.

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The reduction product is crushed, treated first with a large volume of water and then with dilute acids (acetic, nitric, or hydrochloric), washed with water, and vacuum-dried at 40 to 50°.

In order to reduce the oxygen concentration in the powder to about 0.2% it is necessary to carry out a second reduction of the powder by calcium. Even after the second reduction the metal is characterized by greater hardness and lower ductility as compared with titanium produced by the reduction of $TiCl_4$; this is a result of its higher oxygen and nitrogen contents.

Titanium produced by thermal reduction with calcium has the following composition: 98.5 to 99.0% Ti, 0.03 to 0.15% N, 0.2 to 0.4% O, 0.01 to 0.03% H, 0.1 to 0.2% Si, 0.01 to 0.05% C, 0.10 to 0.25% Fe, 0.05 to 0.15% Al, 0.1 to 0.3% Ca, < 0.03% Mg, 0.01 to 0.1% Cu.

Titanium powders produced by the reduction of TiO_2 with calcium are used for the manufacturing of solid titanium bars and products by powder metallurgy methods and for the production of alloys of titanium and other metals. Moreover, they may be used as the starting material for the production of high-purity titanium by thermal dissociation of titanium iodide or by electrolytic refining (see below).

Reduction by calcium hydride

The reduction by calcium hydride (CaH_2) is a variant of the thermal reduction of TiO_2 with calcium.

Calcium hydride is produced by the action of dry hydrogen on calcium at 400 to 600°. The hydride decomposes above 800°, yielding calcium and hydrogen. The nascent atomic hydrogen instantaneously combines into hydrogen molecules. At 970° the equilibrium hydrogen pressure over the hydride is almost one atmosphere.

The reduction of TiO_2 by calcium hydride involves the following over-all reaction:

$$TiO_2 + 2CaH_2 \rightarrow TiH_2 + 2CaO + H_2.$$

The change in the free energy of the reaction at 1000° is $\Delta F_{1000^\circ} = -66.1$ kcal.

Meerson and Kolchin, who studied the chemistry of the process, showed that the main reducing agent is calcium rather than atomic hydrogen (as was previously assumed).

In contrast with the thermal reduction by calcium, the reduction yields titanium hydride or a solid solution of hydrogen in titanium. This is an advantage since in the leaching of the calcium oxide the titanium hydride powder is oxidized to a lesser extent than is titanium powder.

When pellets made of compressed titanium hydride are sintered in vacuo, the hydride decomposes with the evolution of atomic hydrogen which causes partial reduction of the oxide films and thus reduces the oxygen content of the metal.

Calcium hydride is readily decomposed by atmospheric moisture:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2.$$

Hence, it must be stored as lumps in hermetically sealed containers, and the crushing and charge mixing ($TiO_2 + CaH_2$) must be carried out in sealed mills and mixers.

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The reduction process is carried out in equipment made of refractory steel, which is charged with the pelletized titanium dioxide — calcium hydride mixture. The air in the reactor is evacuated and the reactor is filled with dried hydrogen and heated to 900 to 1100°. The powder produced is washed with water and dilute acids (hydrochloric or acetic) to remove the excess calcium and calcium oxide.

Powdered titanium hydride is mainly used in the powder metallurgy of titanium.

50. ELECTROLYTIC REFINING OF TITANIUM AND TITANIUM-BASED ALLOYS

A large proportion of the total cost price of titanium produced by thermal reduction methods is constituted by the cost of the reducing agents (magnesium or sodium) which are manufactured by electrolysis of molten chlorides.

The cost price of titanium may be substantially cut by replacing the thermal reduction methods by direct electrolytic processes. Extensive research is being carried out on the subject, but there is as yet no electrolytic method for the production of titanium which could compete with the manufacturing processes currently used. On the other hand, electrolytic refining of titanium (e.g., of low-quality sponge, or titanium melting wastes) and titanium-based alloys can be carried out. The electrolytic refining of titanium is already used in some industrial plants.

In the electrolytic refining, the impure titanium is used as the anode and is inserted into the molten electrolyte. During the electrolysis, the titanium anode dissolves in the melt and is then deposited on the steel cathode.

Molten alkali metal chlorides (NaCl or a NaCl — KCl mixture) containing 1.5 to 5% of dissolved lower titanium chlorides ($TiCl_2$, $TiCl_3$) are used as the electrolyte. The electrolyte is prepared by the reduction of $TiCl_4$ with sodium or titanium scrap in molten sodium and potassium chlorides.

During the anodic dissolution the titanium passes into the electrolyte in the form of Ti^{2+} and, to a certain extent, Ti^{3+} ions:

$$Ti - 2e \rightarrow Ti^{2+},$$
$$Ti^{2+} - e \rightarrow Ti^{3+}.$$

The reverse reactions take place on the cathode:

$$Ti^{3+} + e \rightarrow Ti^{2+},$$
$$Ti^{2+} + 2e \rightarrow Ti.$$

The main impurities in the crude titanium are oxygen, nitrogen, carbon, iron, and silicon. Titanium-based alloys also contain various alloying additives — Al, Cr, Mn, V, Mo, and Sn.

The electrolytic refining of titanium is based on the difference between the electrode potentials of titanium and the contaminants. During the anodic

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dissolution of titanium the oxygen present as impurity remains in the anodic slag as titanium oxides (TiO_2, Ti_2O_3). The carbon in a free state remains on the surface of the electrolyte or in the form of carbide in the anodic residue; the nitrogen remains in the anodic residue as nitride, or is evolved as gas at the anode; silicon is evolved with the gases as $SiCl_4$; the iron and the nobler metals (Ni, Cu, Sn) accumulate in the anodic residue. The anodic dissolution potentials of several alloying additives (Al, Cr, Mn, V) are close to that of titanium. Thus, they pass into the molten chloride and, when their concentration reaches a certain level, they may be deposited on the cathode together with the titanium.

The refining conditions depend on the content of impurities. When various elements are present together, they have a combined effect on the anodic dissolution. The removal of impurities such as O, N, C, Fe, and Si and of the alloying additives Mo and Sn is easiest. It is more difficult to remove V, Al, and Mn present as impurities. These elements may be removed by twice-repeated refining.

Electrolyzers with packed anodes are the ones most often used in electrolytic refining. A diagram of such electrolyzer is shown in Figure 105. The metal to be refined (in the form of turnings or granules, 2 to 3 mm in size) is placed in a perforated steel basket which serves as the anode. When a deposit of titanium accumulates on the cathode, the cathode is raised into the upper chamber, a discharge pallet is placed underneath and the deposit is cut out with a special knife.

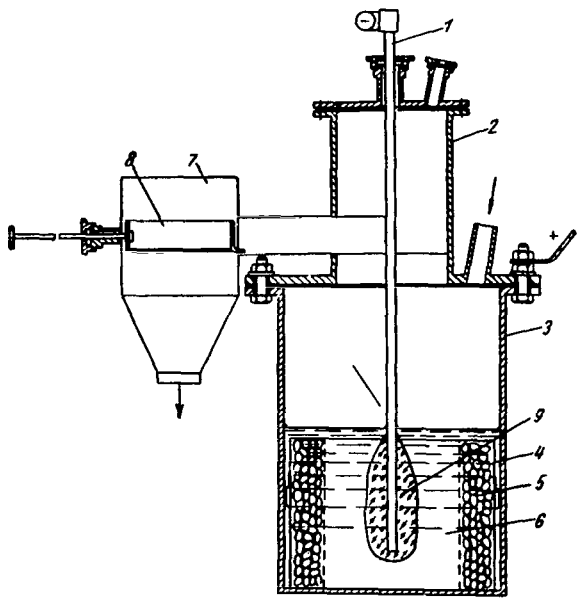

FIGURE 105. Diagram of electrolyzer used for electrolytic refining of titanium.

1—stainless steel cathode; 2—chamber for the removal of the cathodic deposit; 3—body of the electrolyzer (anode); 4—basket for the packed anode; 5—anodic titanium; 6—electrolyte; 7—discharging device; 8—pallet; 9—cathodic deposit.

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The electrolysis is carried out at 850° in an argon atmosphere, at an anodic current density of 0.1 to 0.5 amp/cm^2 (depending on the composition of the titanium to be refined) and a starting cathodic current density of 0.5 to 1.5 amp/cm^2. A coarse crystalline deposit of titanium forms on the cathode. The current efficiency is 90% and higher.

The use of electrolytic refining for the purification of crude titanium produced by direct reduction of titanium slags (e. g., by aluminum or magnesium) is of great interest. Research on the subject is now in progress.

51. REFINING OF TITANIUM BY THE IODIDE PROCESS

Small amounts of extremely pure ductile titanium were produced as early as 1925 by van Arkel and de Boer. Their method was based on the thermal decomposition of gaseous TiI_4 on a surface (e. g., an incandescent tungsten or titanium wire) heated to a high temperature (1300 to 1500°), which resulted in the deposition of the titanium on that surface.

At present, the thermal dissociation of titanium iodide is used for small scale production of high-purity titanium.

The iodide process for the refining of titanium may be represented by the following scheme:

$$\underset{\text{(contaminated)}}{Ti} + 2I_2\,(\text{vapor}) \xrightarrow{100-200^\circ\,C} \underset{\text{(vapor)}}{TiI_4} \xrightarrow{1300-1500^\circ\,C} \underset{\text{(pure)}}{Ti} + 2I_2\,(\text{vapor}).$$

Titanium reacts with iodine at a low temperature (100 to 200°). The gaseous titanium iodide is then made to dissociate on the surface of a wire heated to 1300 to 1500°. The iodine freed in the dissociation again reacts with the contaminated titanium, at a lower temperature, which is present in the vessel. A layer of pure titanium is gradually deposited on the surface of the wire. Dense rods or coarsely crystalline, less dense deposits are obtained, depending on the process conditions.

The elimination of oxygen and nitrogen during the refining of titanium by the iodide process is due to the fact that titanium oxides and nitrides do not react with iodine at the low temperatures required for the formation of TiI_4.

Equipment

The iodide process was originally carried out in glass containers with tungsten terminals (which do not react with the iodine) sealed into the glass. A titanium filament was suspended between the leads, and heated by electrical current supplied to the terminals. The purified titanium was deposited on the bottom and walls of the container.

Industrial scale refining of titanium by the iodide process is now carried out in metal installations. One of the designs used is shown in Figure 106 /22/. The body of the apparatus is made of chromium-nickel alloy (80% Ni, 20% Cr) which is resistant to iodine and TiI_4. Crude titanium powder or turnings are placed along the inner walls of the apparatus in the circular gap formed by a cylindrical screen of molybdenum gauze.

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Titanium wire 3 to 4 mm in diameter (in the form of U-shaped loops) is stretched with the aid of tungsten hooks fastened to steatite insulators. The total length of the filament is about 11 meters. The ends of the filament are fastened to molybdenum terminals.

The airtight lid is fitted with a socket holder for the glass ampoule containing the iodine, and with sleeve connections to the vacuum pump. The retort is placed in a thermostat which maintains the temperature of the titanium undergoing purification at the desired level (between 100 and 200°). The reactor is first evacuated to a residual pressure of $2 \cdot 10^{-4} - 5 \cdot 10^{-5}$ mm Hg. The reactor is then disconnected from the evacuation system and the iodine is introduced. In order to introduce the iodine, a special device is used to break the drawn-out tip of the ampoule.

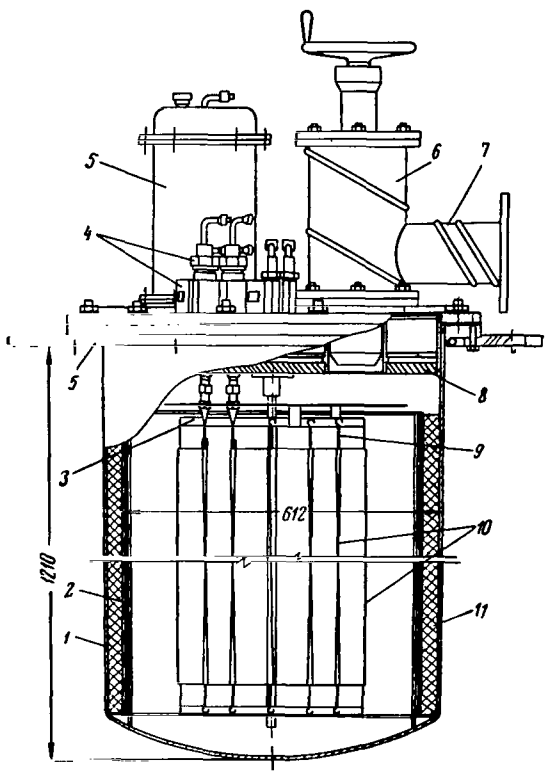

FIGURE 106. Apparatus for the production of titanium by thermal dissociation of titanium iodide.

1 — body of the apparatus; 2 — molybdenum screen; 3 — support of titanium filament; 4 — terminals; 5 — thermostat, with glass ampoule containing iodine; 6 — vacuum lock; 7 — sleeve connection to the vacuum system; 8 — lid; 9 — molybdenum hooks; 10 — titanium filaments; 11 — titanium sponge.

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Electric current is then applied to the filament. The amount of iodine introduced into the reactor is determined by the optimum pressure of the iodine vapor. In practice, the amount of iodine added is 7 to 10% of the amount of titanium to be refined.

The installation is designed to produce 24 kg of refined titanium per working cycle, or 10 kg per day.

Procedure

Refining titanium by the iodide process comprises the following stages:

1) interaction of titanium and iodine at low temperatures (100 to 200°) with the formation of TiI_4:

2) transport of titanium iodide vapors to the surface of the heated filament;

3) decomposition of the iodide on the surface of the filament, at 1300 to 1500°;

4) transport of iodine vapors from the filament to the crude titanium.

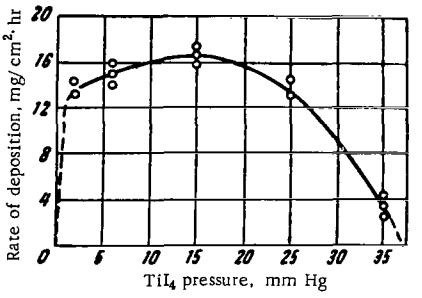

FIGURE 107. Rate of deposition of titanium at a filament temperature of 1500°, as a function of the vapor pressure of TiI_4.

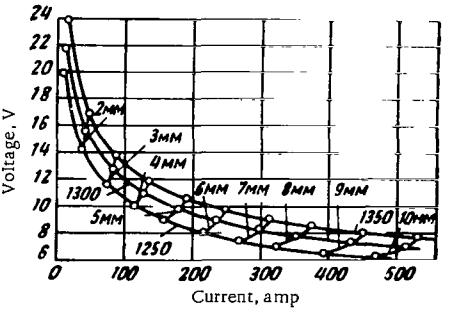

FIGURE 108. Voltage-current curves for the deposition of iodide titanium at various deposition temperatures.

Investigations have shown that the process rate is determined by stages 2 and 4, i. e., by the rate of transport of the iodide to the filament and of the iodine to the raw titanium.

The rate of transfer of the iodide depends mainly on the vapor pressure TiI_4 in the vessel, determined by the temperature of the reactor walls. As is evident from Figure 107, at a filament temperature of 1500° the rate of deposition is at the maximum at iodide pressures from 2 to 20 mm Hg, which corresponds to a reactor-wall temperature between 140 and 200°. The rate of deposition of titanium decreases at higher iodide pressures since the degree of dissociation of iodide then becomes smaller /34/.

Although the maximum rate of deposition corresponds to a wall temperature of 140 to 200°, the process is also fairly rapid at 100°. The maintenance of a constant temperature is then accomplished simply by immersing the reactor in boiling water.

The temperature of the filament is the second factor affecting the rate of the deposition. The rate of deposition is highest at 1500°. Vacuum

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vaporization of titanium is observed at higher temperatures. The filament temperature is usually maintained at 1300 to 1400° in order to prevent the fusion of the filament.

One serious difficulty is to maintain a constant temperature on the filament surface during the accumulation of the deposit. Neglecting the heat losses by heat conductance through the electrodes and by convection (which are relatively small), we may assume that the electrical energy supplied serves to compensate for the heat lost by radiation emitted by the surface of the filament on which the titanium is deposited. In order to maintain the temperature of the filament constant as its diameter grows, it is necessary that the current intensity and the voltage be so adjusted that the power radiating from unit incandescent surface remains constant. The following equation must then be satisfied:

where $IE^3 = K = \text{const},$

I is the current intensity;
E is the voltage.

The above equation is easily derived. The maintenance of a constant temperature requires that

$$\frac{W}{S} = C = \text{const},$$

where $W = IE$ is the radiating energy;
$S = \pi DL$ is the filament surface (D — diameter, L — length);
$C = e\,\sigma T^4$ is the energy radiated by unit surface at the given temperature;
e is a coefficient showing the ratio of the true to the radiation temperature;
σ is the Boltzmann constant.

The total power radiated by a filament of a length L is:

$$W = IE = C\pi DL. \tag{1}$$

The resistance of the filament is:

$$R = \frac{E}{I} = \frac{\rho L}{\frac{\pi D^2}{4}}, \tag{2}$$

where ρ is the specific resistance squaring equation (1) and combining it with equation (2) we obtain

$$IE^3 = 4\pi\rho C^2 L^3.$$

At a given temperature and filament length, the right-hand side of the equation is constant. Hence

$$IE^3 = K = \text{const}.$$

The value of $K = 4\pi\rho\, C^2 L^3$ may be determined if the specific radiation power C and the specific resistance ρ are known. For titanium at 1350° $C = 21.8\ \text{watt/cm}^2$ and $\rho = 240 \cdot 10^{-6}$ ohm · cm.

The effect of the voltage on the current is plotted as a curve (the voltage-current curve) from the calculated value of K; this curve is used to control the process. The voltage-current curve for 1350° is shown in Figure 108 /22/.

Under conditions adopted in industrial practice, the growth rate of the titanium rod is about 10 to 20 mm/day.

A comparison between the concentrations of impurities in titanium made by the iodide process and in titanium made by thermal reduction with magnesium is shown in Table 36.

As compared with titanium made by thermal reduction with magnesium, iodide-refined titanium contains lower amounts of oxygen, nitrogen, iron,

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magnesium, and manganese. The mechanical properties of both types of titanium are listed in Table 27. The titanium refined by the iodide process is much more ductile.

TABLE 36

Composition of titanium made by the iodide process and by thermal reduction with magnesium, in %.

Element	Iodide titanium	Titanium sponge (reduced with magnesium)	Element	Iodide titanium	Titanium sponge (reduced with magnesium)
Carbon	0.01—0.03	0.01—0.03	Magnesium	0.0015—0.002	0.04—0.12
Oxygen	0.005—0.01	0.05—0.15	Manganese	0.005—0.013	0.03—0.06
Nitrogen	0.001—0.004	0.01—0.05	Molybdenum	0.0015	—
Aluminum	0.013—0.05	< 0.005	Nickel	0.003	—
Copper	0.0015—0.002	< 0.03	Silicon	0.03	< 0.01
Iron	0.0035—0.025	0.03—0.2	Tin	0.001—0.01	< 0.03

52. PRODUCTION OF SOLID TITANIUM

The titanium sponge or powder prepared by one of the methods described above is converted into solid, ductile titanium by melting in an arc furnace or by powder-metallurgy techniques.

The melting process is the most widely used; large ingots, weighing from one to four tons may be produced in this way. Powder metallurgy techniques are used for the manufacture of small bars or parts.

The melting of titanium /1, 3, 6, 23, 24/

The melting of titanium is made difficult by the rapid reaction of titanium with gases and by the interaction of the molten metal with all known refractory materials.

In the early development of titanium production, the titanium sponge was melted in induction furnaces with graphite crucibles, in argon atmosphere or in vacuum. However, even the relatively small amount of carbon absorbed by the titanium during the melting (0.25 to 0.8%) impairs its physical and mechanical properties to a considerable extent. Hence, a titanium-melting method which was subsequently developed and which is now extensively used consists of arc-melting in a cooled copper crucible.

The melting is carried out in vacuum arc-melting furnaces with consumable electrodes, whose operation and design have been described in Chapter II.

The vacuum melting resulted in a reduction of the hydrogen concentration in titanium ingots to 0.001 to 0.002% (the hydrogen concentration in titanium melted in argon was about 0.02%), with consequent improvement of the mechanical properties of titanium, and especially of its impact strength.

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Various types of furnaces with consumable electrodes are used for the melting of titanium. In the most widely used types of furnaces the consumable electrode of the desired length is prepared outside the furnace and is then inserted in the furnace which contains a long, water-cooled copper mold (Figure 109). The consumable electrode is welded to the electrode holder (arm) which serves to supply the current to the electrode and to move it during the melting.

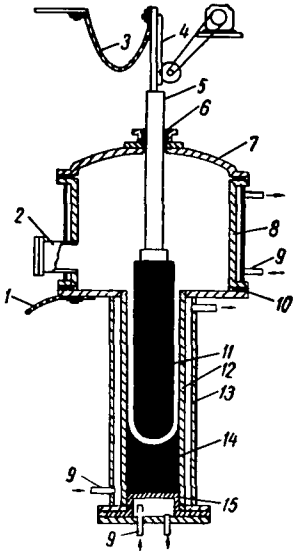

FIGURE 109. Diagram of electric-arc furnace with consumable electrodes.

1—current leads to the mold; 2—sleeve connection to vacuum; 3—flexible bus bar supplying the current to the electrode; 4—device for lifting the electrode; 5—electrode holder (arm); 6—vacuum seals; 7—lid; 8—furnace body; 9—water inlet and outlet tubes; 10—rubber seals; 11—consumable titanium electrode; 12—cooled copper mold; 13—water jacket; 14—ingot; 15—cooled bottom of the mold.

As a safety precaution, arc furnaces are mounted in a chamber with thick reinforced concrete walls and ceilings. The control panel is located behind a concrete wall.

The consumable electrodes are prepared by pressing titanium sponge (particle size 5 to 30 mm) or powder in hydraulic presses fitted with steel dies, under pressures of 2 to 4 tons/cm^2. In most cases the titanium is pressed into cylindrical pellets of small height (diameter 500 mm) which are then welded together in an argon arc into electrodes of the desired length. In some cases the pellets are joined together to form the consumable electrode by sintering with the aid of contact heating in the melting furnace itself. To accomplish this, the pellets are put in the furnace one over the other. The furnace is evacuated, the electrode holder is welded to the upper pellet and a pressure of about one ton is applied to the pellet column by means of the feed mechanism. The current from the generators used for the melting is then turned on. The contact sites between the pellets, which have a high resistance, are rapidly heated to about 800°. At this temperature and pressure the pellets rapidly sinter and cohere. The sintering is accompanied by partial degassing of the pellets (i. e., elimination of dissolved hydrogen, magnesium, and other volatile impurities).

In a vacuum of about 0.1 to 0.01 mm Hg, an arc may be formed because of the presence (in the narrow gap between the consumable electrode and the melt) of ionized vapors of titanium and gaseous impurities and metals evolved during the melting (sodium, magnesium).

It is recommended that the melting be carried at a residual pressure (in the furnace chamber, i. e., in the space above the melting crucible) of 0.01 mm Hg. Under these conditions the actual pressure in the crucible (at the molten metal level) is always higher and attains about 0.1 mm Hg.

The selection of vacuum pumps for the arc furnace will be determined by the necessity for evacuating the gases evolved and for maintaining a certain vacuum. The magnitude of the gas flow created during the melting

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depends on the concentration of volatile substances in the sponge and on the melting rate. Thus, at a melting rate of 5 kg/min the gas flow is:

Concentration of gases in the sponge, l/kg	0.25	1	2
Gas flow*, mm Hg l/sec.....	15.9	63.4	126.8

Vacuum arc furnaces may operate on alternating or direct current, but furnaces operating on direct current (in which the electrode serves as the cathode and the melt as the anode) are preferred. In DC furnaces the melting consumes about 2/3 of the total amount of energy, and in AC furnaces about 1/2. As a consequence, a larger volume of the metal is in the molten state and favorable conditions are created for the production of a uniform ingot.

The current is rectified with the aid of motor generators or (which is much more convenient) with selenium or germanium rectifiers. A current of 8000 to 9000 amp at 25 to 30 V is used for ingots 350 mm in diameter. Under these conditions the melting rate varies between 3.7 and 4.5 kg/minute. The consumption of electrical energy is about 4.5 to 4.8 kwh/kg titanium.

A stable arc discharge must be maintained during arc melting, and formation of secondary arcs between the electrode and the crucible walls as well as the glow discharge must be prevented. Glow discharge is observed between the arc electrodes at a certain critical pressure of the gases. During the glow discharge the arc between the electrodes is extinguished and the discharge takes place through the bulk of the ionized gas, in the entire volume of the crucible. The glow discharge is accompanied by a strong luminescence of the gas.

A magnetic coil (solenoid) fitted off-center with respect to the crucible is used to stabilize the arc in the vacuum. The external magnetic field presses the secondary arcs against the crucible walls (as concentric rings) and they become so long that the applied voltage is not sufficient to maintain them. Moreover, the presence of the magnetic coil results in the mixing of the metal, which improves its uniformity.

Secondary arcs between the electrode and the crucible walls are observed during the gas ionization caused by the spattering of the molten titanium. The spattering may be reduced to a minimum by working at a small distance between the electrode and the melt (5 to 10 mm) and using a narrow gap between the electrode and the crucible wall (20 to 30 mm). Moreover, the spattering impairs the quality of the ingot surface, since droplets of the metal solidify on the crucible walls without joining the bulk of the ingot, which must be machined to a considerable depth, thus reducing the useful yield of the metal. The losses are often as high as 10 to 15%.

The melting of titanium alloys

The refractoriness and mechanical properties of titanium are improved by the addition of alloying additives (manganese, aluminum, chromium, vanadium, molybdenum, iron, and other metals) in concentrations of a few percent.

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* In vacuum technology the gas flow has the dimensions $p \cdot V/t$ where p is the pressure, V the volume and t the time.

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Since only a small amount of the metal is in the molten state during arc melting, it is difficult to ensure the uniformity of the alloy. It is advisable to mix the alloying additive with the sponge before pressing the consumable electrode. A less satisfactory method consists in a uniform distribution over the melting zone of pellets made of the alloying additives.

In all these methods, the production of a uniform alloy requires a second melting, in which the ingot produced by the first melting is used as the consumable electrode.

Production of solid titanium by powder metallurgy techniques /2/

Solid ductile titanium may be produced by powder metallurgy techniques, provided the oxygen and nitrogen contents of the starting powder do not exceed the maximum permissible limit.

The starting materials used in the production of titanium by powder metallurgy techniques are titanium produced by thermal reduction with calcium hydride (see Section 49) or by grinding a titanium sponge.

Titanium sponge is ductile, which makes grinding difficult. Most often titanium sponge is converted to a powder by saturation of the sponge with hydrogen; titanium hydride is then formed, which is brittle and is readily ground. The saturation with hydrogen is carried out in hermetically sealed steel reactors. The sponge is first heated in vacuum to 800°, then cooled to 400 to 450° and purified (nitrogen- and oxygen-free) hydrogen is admitted. At first the reaction is quite vigorous and is accompanied by the evolution of heat. Hence, the hydrogen must be admitted gradually, and must be diluted in the first stage with an inert gas.

Very brittle titanium hydride is obtained when the hydrogen content attains 3 to 4%. The hydride is ground in ball mills to a particle size of 0.05 to 0.12 mm. This corresponds to a powder with an average specific surface of 740 cm^2/g. Finer hydride powders actively absorb nitrogen and oxygen.

Powdered titanium hydride, being more brittle, is more difficult to press than the powders obtained by grinding the sponge. The bars obtained are less strong but are sintered more rapidly than bars made of non-hydrogenated titanium powder. Titanium or titanium hydride bars are pressed in steel dies under pressures from 3.5 to 8 $tons/cm^2$.

Large bars weighing 50 kg or more are most conveniently pressed by the use of the hydrostatic technique discussed in the chapter "Molybdenum".

The sintering is carried out at 1000 to 1300° in vacuo (10^{-4} mm Hg). The satisfactory sintering obtained at these relatively low temperatures may be attributed to a certain extent to the fact that an $\alpha \rightarrow \beta$ transformation (i.e., the conversion of the hexagonal form of titanium into the cubic form) takes place at 880°, which increases the mobility of the atoms. Moreover, the sintering of titanium hydride is favored by the dissociation of the hydride (which takes place at these temperatures), which also increases the mobility of the atoms.

During the sintering of bars made of titanium hydride powders, the bulk of the hydrogen is evolved at 500 to 800°, which means that the temperature rise in this range must be slow. The temperature is then increased to 1200 to 1300°.

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The final porosity of articles made of titanium hydride does not exceed 2%, the linear contraction being 12 to 14%. Thus, the density of articles made of pressed titanium hydride (density when pressed 3.2 to 3.8 g/cm^3) sintered for 8 hours at 1300° increases to 4.45 g/cm^3. Because of the large contraction during the sintering, hydride powders cannot be used for the production of standard size articles.

The linear contraction during sintering (for 15 hours at 1000° and 4 hours at 1200°) of coarse titanium powders produced by the grinding of titanium sponge is only 4 to 5%. The production of solid metal involves intermediate forging (compression) of the metal followed by a second sintering.

One of the advantages of powder metallurgy is that the resulting alloys are uniform. The pulverized alloying constituents must be throughly mixed before pressing with titanium or titanium hydride powder.

Large bars weighing 50 to 60 kg may be sintered in vacuum induction furnaces.

In addition to the conventional powder metallurgy method, another method used in titanium metallurgy consists of combined pressing, sintering, and mechanical treatment under pressure. A description of the method is given below. The titanium powder is tightly packed in a steel tube, the tube ends are sealed by welding, and the tube with the powder is hot-rolled at 900°. The steel shell protects the metal against oxidation. After the rolling the steel shell is cut and is readily separated from the titanium sheet as a result of the formation of a thin intermediate layer of a titanium-iron alloy.

The mechanical properties of titanium produced by powder metallurgy techniques are virtually the same as those of arc-melted titanium. However, powder metallurgy cannot supersede the melting method because of the limited dimensions of the bars. The powder metallurgy method is more suited to mass production of small sized titanium and titanium-alloy articles. Its advantages are: the economical utilization of the metal (finishing operations are few), production of articles of any desired density, and the production of uniform alloys.

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Chapter V

ZIRCONIUM

53. GENERAL DATA ON ZIRCONIUM

Zirconium belongs to Group IV of the periodic system. It was discovered by Klaproth in 1789 in its most abundant mineral — zircon. This mineral has been known since antiquity and has been used as a precious stone under various names (hyacinth, jacinth, jargon).

Berzelius was the first to prepare metallic zirconium (in 1824) in the form of a very impure powder, by reduction of potassium fluorozirconate with potassium.

Pure ductile zirconium was prepared only in 1925 (i. e., 136 years after the discovery of the element) by thermal dissociation of zirconium iodide. This complex process, which was developed by van Arkel and de Boer, was until recently the only available method for the production of ductile zirconium. Methods for large-scale production of ductile zirconium have only been developed in the last decade.

Zirconium compounds and metallic zirconium produced from ores always contain hafnium (the chemical analog of zirconium, which was discovered in 1923) as an impurity. The concentration of hafnium in the zirconium depends on the nature of the starting raw material and ranges from a fraction of one percent to several percent.

Properties of zirconium /1, 2/

The appearance of solid zirconium resembles that of steel; zirconium powder has a dark-gray color.

Zirconium appears in two crystalline forms: the hexagonal α = form (lattice parameters $a = 3.223$ Å, $c = 5.123$ Å), which is stable up to 862°, and the face-centered cubic form β (lattice parameters $a = 3.61$ Å), which is stable above 862°.

Hafnium exists in the same forms. However, the transition from the α- to the β-form of hafnium takes place at a higher temperature (1310 ± 10°).

Some of the physical properties of zirconium and its analog, hafnium, are given in Table 37.

Pure zirconium is ductile and can be readily worked by forging, rolling into sheets, and drawing. The presence of oxygen, nitrogen, carbon and hydrogen strongly affects the properties of zirconium, and its properties therefore depend on the method of production of the metal (see Table 42).

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TABLE 37

Physical properties of zirconium and hafnium

Property	Zirconium	Hafnium
Atomic number	40	72
Atomic weight	91.22	178.6
Density, g/cm^3	6.52 (for α-Zr)	13.3 (for α-Hf)
Melting point, °C	1852 ± 10°	2130 ± 15°
Boiling point, °C	~ 3600	~ 5400
Transition temperature to superconducting state, °K	0.7	0.35
Specific heat, cal/g, °C		
25—100°	0.066	0.035
1000—1500°	0.113	—
Linear expansion coefficient	$89 \cdot 10^{-7}$ (at 20—700°C)	$59 \cdot 10^{-7}$ (at 0—1000°C)
Total radiation ($watt/cm^2$) at various temperatures, °C		
927	2.03	—
1127	5.40	—
1227	7.20	—
1327	10.0	—
Electrical resistivity, ohm·cm, at °C:		
20	$41 \cdot 10^{-6}$	$34 \cdot 10^{-6}$
800	$143 \cdot 10^{-6}$	—
Thermal neutron capture cross section, barns	0.18 ± 0.02	115 ± 5

Zirconium is stable in air. When the solid metal is heated to 400 to 600°, it is coated with an oxide film, but above 800° it becomes rapidly oxidized with the formation of the higher oxide ZrO_2. Zirconium powder is oxidized in the air with spontaneous ignition at 180 to 285° (depending on the particle size).

Zirconium actively absorbs hydrogen at temperatures as low as 300 to 400°, with the formation of a solid solution of hydrogen in zirconium and of zirconium hydrides (Zr_2H, ZrH, and ZrH_2). The hydrogen can be expelled from the metal by heating to 1200 to 1300° in a high vacuum.

Above 900° zirconium rapidly absorbs nitrogen and reacts vigorously with carbon monoxide. Zirconium forms very hard and refractory compounds with nitrogen and carbon — the nitride ZrN (mp 2930°) and the carbide ZrC (mp 3530°).

In contrast to hydrogen, oxygen and nitrogen cannot be removed from zirconium by heating in vacuo.

The corrosion resistance of zirconium is superior to that of titanium and approaches that of tantalum and niobium. Thus, below 100° zirconium resists hydrochloric and nitric acids of all concentrations and of sulfuric acid of concentrations up to 50%.

Zirconium is resistant to aqua regia at room temperature, dissolves in hydrofluoric acid and in concentrated sulfuric acid at 100°, but is not dissolved by aqueous solutions of alkali hydroxides.

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Chemical properties /17/

Compounds of tetravalent zirconium are the only ones of practical importance; lower valency compounds are unstable and have been inadequately studied.

Zirconium dioxide. Zirconium dioxide ZrO_2 is produced by ignition of zirconium hydroxide or other zirconium salts — sulfates, nitrates. The pure dioxide is white. After the ignition, ZrO_2 is virtually insoluble in hydrochloric, nitric and dilute sulfuric acids. The dioxide dissolves in hydrofluoric and in hot concentrated sulfuric acids.

Zirconium dioxide is very stable and has refractory properties. The heat of formation of ZrO_2 is 259.5 kcal/mole, its melting point is 2700 to 2900°. ZrO_2 exists in several crystalline modifications. The monoclinic form is stable up to 1000 to 1100°, the tetragonal at 1100 to 1900°, and the trigonal above 1900°.

Zirconium dioxide is amphoteric. The fusion of ZrO_2 with alkalies yields zirconates (salts of zirconic acid), while the dissolution of the dioxide in acids results in the formation of the respective salts — zirconium sulfates, chlorides and nitrates. In aqueous solution these salts hydrolyze with the formation of zirconyl (ZrO^{2+}) salts, e.g.:

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl.$$

Zirconates. Salts of metazirconic (H_2ZrO_3) and orthozirconic (H_2ZrO_4) acids are known. Most zirconates are insoluble in water.

Sodium and potassium zirconates are produced by the fusion of ZrO_2 with alkali hydroxides, sodium carbonate or potassium carbonate. They are sparingly soluble in water, but undergo hydrolytic decomposition by reactions of the type:

$$Na_2ZrO_3 + 2H_2O \rightleftarrows ZrO(OH)_2 + 2NaOH.$$

Calcium and magnesium zirconates ($CaZrO_3$ and $MgZrO_3$) are produced by heating a mixture of ZrO_2 with CaO or MgO powders to 1400 to 1600°. The melting points of calcium and magnesium zirconates are 2350 and 2150° respectively.

Sulfates. The anhydrous zirconium sulfate $Zr(SO_4)_2$ (a white crystalline substance) is formed when ZrO_2 is heated with concentrated sulfuric acid. Its dissolution in water is accompanied by hydrolysis and complex-formation:

$$Zr(SO_4)_2 + H_2O \rightleftarrows (ZrO)SO_4 + H_2SO_4,$$
$$ZrO(SO_4) + H_2SO_4 \rightleftarrows H_2[ZrO(SO_4)_2] — \text{zirconylsulfuric acid.}$$

Upon evaporation of the sulfuric acid solution, zirconylsulfuric acid crystallizes out as the trihydrate $H_2[ZrO(SO_4)_2] \cdot 3H_2O$.

The formula of the normal zirconium sulfate $Zr(SO_4)_2 \cdot 4H_2O$ is occasionally incorrectly ascribed to the trihydrate; from the standpoint of chemical composition both formulas are identical.

When a weakly acid solution containing zirconyl sulfate is boiled, hydrolysis takes place with the formation of sparingly soluble basic zirconium sulfates whose composition can be expressed by the general formula $xZrO_2 \cdot ySO_3 \cdot zH_2O$.

In the basic sulfates the molar ratio $ZrO_2 : SO_3 > 1$.

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Halides. Zirconium chloride and oxychloride. Zirconium tetrachloride $ZrCl_4$ is one of the starting materials for the production of zirconium metal. The chloride is formed as a result of the high-temperature interaction of chlorine with a mixture of zirconium dioxide and carbon or zirconium carbide:

$$ZrO_2 + 2C + 2Cl_2 = ZrCl_4 + 2CO;$$
$$ZrC + 2Cl_2 = ZrCl_4 + C.$$

The chloride is a white crystalline powder which sublimes at low temperatures. The vapor pressure over the solid salt is 1 atm at 330°.

The salt melts at 437° under a pressure of 18.7 atm. The heat of formation of solid $ZrCl_4$ is 231.9 kcal/mole, the heat of sublimation is 28.5 kcal/mole. Zirconium chloride is very hygroscopic and is hydrolyzed in aqueous solutions (and in humid air) with the formation of zirconium oxychloride $ZrOCl_2$ (zirconyl chloride).

Zirconium oxychloride is stable in aqueous solutions. It crystallizes out as the crystalline hydrate $ZrOCl_2 \cdot 8H_2O$. The crystals are in the shape of tetragonal prisms with well-defined cleavage. The salt is readily soluble in water and sparingly soluble in concentrated hydrochloric acid (see Figure 113).

$ZrOCl_2 \cdot 8H_2O$ may be dried in air without decomposition. In dry air the hydrate loses some water and is converted into the dihydrate $ZrOCl_2 \cdot 2H_2O$. Quantitative dehydration takes place at 180 to 200°. The heat of formation of anhydrous $ZrOCl_2$ is 246 kcal/mole.

Zirconium bromide and iodide. From the standpoint of their properties $ZrBr_4$ and ZrI_4 resemble zirconium chloride. Like the chloride they are readily sublimed. The vapor pressure over the solid salts attains one atmosphere at 357° for $ZrBr_4$ and at 430° for ZrI_4. At elevated pressures these salts melt at 450 and 499° respectively. Zirconium iodide is used to prepare high-purity zirconium metal by the thermal dissociation method.

Zirconium fluorides and complex fluorides. Zirconium fluoride ZrF_4 is formed by the interaction between gaseous hydrogen fluoride and zirconium dioxide at 500 to 600°, or when zirconium dioxide is heated with acid ammonium fluoride.

$$ZrO_2 + 4HF = ZrF_4 + 2H_2O;$$
$$ZrO_2 + 2NH_4HF_2 = ZrF_4 + 2NH_3 + 2H_2O.$$

Zirconium fluoride is a white substance, which boils at 908°. The heat of formation of ZrF_4 is 456 kcal/mole.

The crystalline hydrate $ZrF_4 \cdot H_2O$ is precipitated on the addition of hydrofluoric acid to a solution of zirconium chloride or sulfate. The fluoride dissolves in the presence of excess hydrofluoric acid; this is due to the formation of the complex acid:

$$ZrF_4 + 2HF \rightleftarrows H_2[ZrF_6].$$

Similarly, the dissolution of zirconium dioxide (or hydroxide) in hydrofluoric acid is accompanied by the reaction

$$ZrO_2 + 6HF \rightleftarrows H_2[ZrF_6] + 2H_2O.$$

Complex salts — fluozirconates K_2ZrF_6 and Na_2ZrF_6 — are formed in solutions containing potassium and sodium ions.

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Potassium fluozirconate is of importance in technology. This salt readily crystallizes out of solutions as colorless rhombic prisms. The solubility of this salt is strongly affected by the temperature (see Table 40), so that it can be purified by recrystallization. The fluozirconate is stable in the air and is not hygroscopic. The salt is used as starting material for the production of metallic zirconium.

Nitrates. Zirconium hydroxide dissolves in nitric acid. Depending on the concentration of the nitric acid, the salt crystallizing out of solution is either the normal nitrate $Zr(NO_3)_4 \cdot 5H_2O$ or zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$ and dizirconyl nitrate $Zr_2O_3(NO_3)_2 \cdot 2H_2O$. In manufacturing processes zirconium is occasionally isolated as zirconyl nitrate.

Phosphates. On the addition of orthophosphoric acid or sodium phosphate to an acid solution of a zirconium compound, a white precipitate of the phosphate $ZrH_2(PO_4)_2$ separates out; it is converted upon ignition into the pyrophosphate ZrP_2O_7. Zirconium phosphate is insoluble in water and in sulfuric and hydrochloric acids of concentrations up to 20%. This makes it possible to separate zirconium from almost all other elements.

Zirconium carbide and nitride. The carbide ZrC and nitride ZrN are very hard, refractory substances with metallic properties (metallic luster, electrical conductivity). The melting point of the carbide is 3530°, that of the nitride is 2930°. The two compounds have the same crystal lattice (f. c. c.) and form a continuous series of solid solutions. The heat of formation of ZrC is 48.2 kcal/mole, that of ZrN is 82.2 kcal/mole.

The carbide is produced by heating a mixture of zirconium dioxide and carbon at 1900 to 2000°, through the reaction:

$$ZrO_2 + 3C = ZrC + 2CO.$$

If the process is carried out in the presence of nitrogen, the carbide produced always contains some nitrogen. Zirconium nitride is formed by the reaction of nitrogen with zirconium powder at 800 to 1000° or between gaseous ammonia and zirconium tetrachloride.

Uses of zirconium /16/

Zirconium, its alloys and chemical compounds are used in various branches of industry. Its main uses at present are:

1) nuclear energetics;
2) electronics;
3) pyrotechnics and manufacture of ammunition;
4) machine building;
5) production of steels and nonferrous metal alloys;
6) production of refractories, ceramics, enamels, and glasses.

Zirconium metal or zirconium-based alloys are used in the first four industries listed above.

Nuclear energetics. In view of the development of nuclear energetics, zirconium attracted attention in 1950 as a possible structural material for nuclear power reactors, with the result that ductile zirconium and zirconium-based alloys began to be manufactured. The value of

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zirconium as a structural material in nuclear technology is explained by its low thermal neutron capture cross section (about 0.2 barn), its high resistance to corrosion and favorable mechanical properties.

The low thermal neutron capture cross section of zirconium was not at first evident, since zirconium usually contains 0.5 to 3% of hafnium which has a much higher capture cross section (about 115 barns). Accordingly, before zirconium could be used in nuclear technology it was necessary to solve the difficult problem of the separation of zirconium from its chemical analog — hafnium.

Zirconium and its alloys are used in nuclear power reactors which operate at temperatures which are too high for the use of aluminum to be possible. Zirconium is used to make protective shells for uranium fuel elements, coolant circulation tubes, and other structural parts. The heat resistance of zirconium and its resistance to the effect of water and steam may be improved by the addition of tin (1.4 to 1.6%) as well as of small amounts of iron (0.1 to 0.15%), chromium (0.08 to 0.12%), and nickel (0.04 to 0.06%). The alloy containing these additives is known as "Zircalloy-2" /1, 2, 16/.

Like molybdenum, zirconium is used for alloying uranium used as nuclear fuel; the addition of zirconium improves the mechanical strength and corrosion resistance of the uranium.

Electronics. The use of zirconium in vacuum tubes is due to its ability to absorb gases, and so to maintain a high vacuum in electronic instruments. For this purpose zirconium powder of ductile zirconium is applied to the surfaces of anodes, grids, and other heated parts of vacuum tubes. The application of zirconium to the surface of grids in radio tubes suppresses grid emission.

Zirconium foil is used in X-ray tubes with molybdenum anticathodes. The foil serves as filter which renders the radiation more monochromatic.

Pyrotechnics and manufacture of munitions. Zirconium powder, which has a low ignition temperature and a high burning rate, is used in this branch of technology.

Zirconium powder is used as the ignitor in mixtures for detonator caps, and in mixtures for photographic flash bulbs. Mixtures of zirconium powder with oxidants (barium nitrate or potassium chlorate) are used as smokeless powder.

Machine building. Until recently ductile zirconium and its alloys were used mainly in nuclear technology. However, with the further increase in its production volume and decrease in price zirconium may be effectively used as material for chemical plant equipment; it is employed as acid-resistant material for the production of centrifuge parts, pumps, condensers, and evaporators; general purpose machine parts (pistons, rods, shafts, etc.) — in turbine building (turbine blades and other parts) — and in the production of medical instruments.

Production of steels and nonferrous metal alloys. Zirconium is extensively used as an additive to steel, serving to deoxidize the steel, to remove nitrogen, and to bind sulfur. In addition, zirconium is a valuable alloying element which is added to certain brands of armor steel, steels for forged gun parts, stainless steels, and high-temperature steels. Zirconium is added to steels in the form of ferrosilicozirconium (40 to 45% Zr, 20 to 24% Si; remainder iron).

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Zirconium is a component of a series of nonferrous alloys (copper, magnesium, lead, nickel base alloys).

Copper alloys containing 0.1 to 5% Zr can be hardened by thermal treatment (quenching and tempering). The tensile strength reaches 50 kg/mm^2, which is 50% higher than that of nonannealed copper. When articles made of pure copper (wires, sheets, tubes) are heated up to 200° their strength decreases considerably because of the release of cold-hardening. The addition of zirconium increases the annealing temperature of copper to 500°. The addition of small amounts of zirconium to copper increases its strength with only an insignificant decrease in the electrical conductivity of the copper. Zirconium is added to copper in the form of a hardening copper-zirconium alloy containing 12 to 14% Zr. Copper-zirconium alloys are used for the production of electrodes for spot welding and for electrical bus bars when a high strength is required.

Mangesium alloys containing zirconium are now increasingly used. The addition of small amounts of zirconium favors the formation of fine-grained magnesium castings and thus increases the strength of the metal. Magnesium alloys with zinc and zirconium are very strong. Magnesium alloy with 4 to 5% Zn and 0.6 to 0.7% Zr does not display creep below 200° and its use as a structural material for jet engines has been recommended.

Zirconium is added (in the form of a silicon-zirconium alloy) to lead bronzes. It promotes the dispersion of lead and completely prevents the segregation of lead in the alloy. Copper-cadmium alloys containing up to 0.35% Zr are characterized by their high strength and electrical conductance.

Zirconium is a component of a number of corrosion-resistant alloys. Thus, an alloy containing 54% Nb, 40% Ta and 6 to 7% Zr has been proposed as a substitute for platinum.

Manufacture of refractories, porcelain, enamels, glazes and glass. These branches of industry at present account for more than 50% of the total consumption of zirconium; zirconium is used in the form of its minerals (zircon and baddeleyite) and chemical compounds (zirconium dioxide, zirconates, zirconium diboride).

Zirconium dioxide (mp 2700 to 2900°) and the mineral zircon ($ZrSiO_4$) are used as refractories.

Pure zirconium dioxide is unsatisfactory as a refractory material because of its thermal instability which causes articles heated to high temperatures to crack upon cooling. This is associated with phase transformations in the dioxide; such transformations are accompanied by volume changes which cause the cracking. The cracking is prevented by the addition of stabilizers — magnesium or calcium oxides. The stabilizers dissolve in the zirconium dioixde forming a solid solution with a cubic crystal lattice, which is stable at both high and low temperatures.

Zirconium dioxide or the minerals zircon and baddeleyite are used in the production of refractory bricks for metallurgical furnaces, crucibles for melting metals and alloys, refractory tubes, and other articles.

Zirconium minerals or zirconium dioxide are added to certain brands of porcelain used for the production of insulators for high-voltage lines, for high-frequency circuits, and for the spark plugs in internal-combustion engines. Zirconium-containing porcelain has a high dielectric constant and a low expansion coefficient.

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Zirconium dioxide and zircon (purified from iron) find extensive use as enamel components. They impart to the enamel a white color and resistance to acids and completely replace tin oxide which is in short supply. Zircon and zirconium dioxide are also components of certain brands of glass. The addition of ZrO_2 improves the resistance of the glass to alkali solutions.

A large proportion of high-quality zirconium concentrates is used in foundry practice for the production of casting molds and rods; powdered zircon is applied to the surface of molds to obtain casts with satisfactory surface properties.

Other uses. Mention should be made of the use of zirconium sulfates (double zirconium ammonium sulfate, etc.) as tanning agents in the leather industry. The total production of zirconium concentrates outside the USSR is about 170,000 tons/year.

Uses of hafnium /16/

The commercial production of hafnium and its compounds is only 6 to 8 years old. Interest in hafnium arose mainly in connection with nuclear technology in which it is a component of the control rods and reactor shields (hafnium has a high thermal neutron capture cross section — 115 barns). It is used as metal, as hafnium dioxide and as hafnium diboride (HfB_2).

Another promising use is in the production of refractory materials. Hafnium carbide (mp 4000°) or a solid solution of hafnium carbide in tantalum carbide (75% TaC) with a mp of 4200° may be used. Other refractory compounds of hafnium are also being studied.

54. MINERALS, ORES, AND ORE CONCENTRATES

The abundance of zirconium in the Earth's crust is 0.025% by weight. In the order of abundance it precedes some common metals such as copper, zinc, tin, nickel, and lead.

There are about 20 known zirconium minerals. They are concentrated mainly in granite and basic (nepheline-syenite) pegmatites.

Zirconium minerals may be divided into three groups:

1) zirconium dioxide (the mineral baddeleyite and its varieties);
2) zirconium orthosilicates (zircon and its varieties);
3) the zirconosilicates of sodium, calcium, iron and other elements (eudialyte, eucolite, catapleite, etc.).

The minerals baddeleyite and zircon are at present the main industrial sources of zirconium. In addition, the minerals eudialyte and eucolite may serve as a source of zirconium but their zirconium content is much lower.

Baddeleyite consists of almost pure zirconium oxide. The common impurity is hafnium (up to a few percent) and more rarely uranium (up to 1%) and thorium (up to 0.2%) as well as mechanical contaminants — minerals containing SiO_2, TiO_2, Fe_2O_3, etc. The purest samples contain

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98 % ZrO_2. Large amounts of baddeleyite have been discovered in Brazil. The mineral is a common impurity in monazite sands (the mineral monazite is a rare-earth phosphate).

Baddeleyite has a density of 5.5 to 6, a Mohs hardness of 6.5, and a mp of 2700 to 2900° (depending on the concentration of impurities, which depress the melting point). The primitive beneficiation methods used in Brazil (washing with water in trenches and manual classification on tables) produce baddeleyite concentrates known as "zircite" which consist of a baddeleyite-zircon mixture containing approximately 75 to 82% ZrO_2, 2 to 5% Fe_2O_3, 6 to 17% SiO_2, 1.3 to 1.7% Al_2O_3 and 0.2 to 0.8% TiO_2.

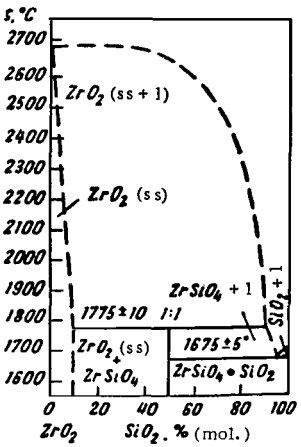

FIGURE 110. Phase diagram of the system ZrO_2—SiO_2.

The major impurities in the concentrates are silica, iron, aluminum, and titanium. High-quality concentrates are produced by gravitational beneficiation on concentration tables (resulting in the removal of the lighter Al-containing minerals) and electromagnetic enrichment (the magnetic iron minerals and ilmenite pass into the magnetic fraction).

Zircon is zirconium orthosilicate $ZrSiO_4$ (67.2% ZrO_2, 32.8% SiO_2). This is the most common zirconium mineral. It is concentrated mainly in the pegmatites of the granitic and especially alkaline magma. It is often found in placers formed by the decomposition of bedrock.

The phase diagram of the system ZrO_2 to SiO_2 (Figure 110) shows that zircon melts (with decomposition) at 1775°. Decomposition of zircon to ZrO_2 and SiO_2 is also observed in the solid state at temperatures above 1540°. A eutectic mixture of zircon and SiO_2 melts at 1675°. Hence, the presence of silica strongly reduces the melting point of zircon.

Zircon is not attacked by inorganic acids (except hydrofluoric acid). It is inert to many molten metals, and reacts only to a small extent with glass and slags.

Zircon usually contains hafnium (0.5 to 4%) as well as Fe_2O_3 (up to 0.35%) and CaO (0.05 to 4%). Some of the rarer varieties contain lanthanides, niobium, tantalum, thorium, and uranium. The mineral is yellow, red-brown, and more rarely green. Colorless varieties also exist. The density of zircon is 4.4 to 4.7, the Mohs hardness is 7.5.

Zircons have a tendency towards the so-called metamict decomposition, in which a crystalline substance vitrifies without a change in the external appearance of the crystal. It is believed that the metamict decomposition of zircon is associated with the rupture of bonds in the zircon lattice caused by the α-radiation emitted by radioactive impurities (uranium, thorium) in the mineral. The metamict transformation occasionally results in a complete decomposition of the zircon into the oxides ZrO_2 and SiO_2.

The main zirconium reserves are found in coastal zirconium placers, where it usually appears together with ilmenite, rutile, monazite, and a number of other minerals.

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Zircon-containing ores are enriched by gravitational methods in conjunction with magnetic and electrostatic separation. The separation of zircon from quartz is carried out by concentration on tables. Ilmenite and garnet (a silicate of aluminum, iron, calcium, and other elements) are separated by magnetic methods with the use of weak fields (zircon is non-magnetic). Monazite is separated by magnetic separation in strong fields. The rutile and the zircon are separated by electrostatic methods or by flotation.

A more complete removal of the iron (which is of importance when the zircon is to be used as a component of enamels) is attained by treating the concentrate with hot sulfuric acid.

The approximate composition of zircon concentrates is shown in Table 38.

TABLE 38

Approximate composition of zircon concentrates,%

ZrO_2	Fe_2O_3	SiO_2	TiO_2
58.44	4.26	31.20	5.5
66.42	1.9	33.0	Traces
61.31	1.4	34.8	1.7
66.3	0.8	31.0	2.3

The largest zircon deposits outside the USSR are in Australia, India, and Brazil.

In the USSR, zircon is found in the Urals, in the Azov alkaline massif, and in other regions.

Eudialyte and eucolite. The composition of eudialyte corresponds to the empirical formula $(Na, Ca)_6Zr[Si_6O_{18}][OH, Cl]_2$. Eucolite is a variety of eudialyte, containing Fe^{2+} ions. A mineral of intermediate composition, mesodialyte, is also known. Eudialyte contains 11.6 to 17.3% Na_2O, 12 to 14.5% ZrO_2, 3.1 to 7.1% FeO, 47.2 to 51.2% SiO_2 and 0.7 to 1.6% Ce. The mineral contains small amounts of rare-earth metals (Ce, La, Y) and niobium.

Eudialyte is colored various shades of pink or crimson. The mineral is readily decomposed by acids.

Eudialyte and eucolite are usually found in alkaline magnatic rocks (nepheline syenites). Deposits are found in the USSR, Norway, Greenland, Transvaal, Brazil, and other countries.

55. PRODUCTS FORMED IN THE PROCESSING OF ZIRCON CONCENTRATES

Zircon concentrates, which are the main zircon raw material, serve as the starting material for the production of ferrosilicozirconium, ferrozirconium and zirconium compounds: zirconium dioxide, potassium fluozirconate and zirconium tetrachloride.

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Ferrosilicozirconium is produced directly by smelting zircon concentrates. Technical zirconium dioxide serves as raw material for the smelting of ferrozirconium and is used for the production of refractories. The high-purity dioxide is used for the production of high-quality refractory articles (crucibles, tubes, etc.).

Potassium fluozirconate and zirconium tetrachloride are used mainly for the production of metallic zirconium.

The main methods for the production of zirconium dioxide, potassium fluozirconate and zirconium chloride from zircon concentrates are reviewed below.

56. METHODS FOR THE DECOMPOSITION OF ZIRCON CONCENTRATES

Zircon is a very stable mineral. It is decomposed by various pyrometallurgical methods by way of decomposition of zirconium silicate.

The following methods are used for the decomposition of zircon:

1. fusion of zircon with sodium hydroxide, with the formation of sodium zirconate;
2. sintering with lime or chalk, with the formation of calcium zirconate;
3. fusion with potassium fluosilicate K_2SiF_6, with the formation of potassium fluozirconate;
4. chlorination of a mixture of zircon and carbon to produce zirconium tetrachloride;
5. reductive smelting with coal to zirconium carbide ZrC, which is chlorinated to produce zirconium chloride.

The first two methods are commonly used for the production of technical and pure grade zirconium dioxide. If necessary, a processing stage involving the separation of hafnium from zirconium is included.

The method of fusion with K_2SiF_6, developed in the USSR, can be readily combined with the separation of zirconium and hafnium by fractional crystallization of the complex fluorides (see Section 63).

The fourth and fifth methods are used in the production of zirconium tetrachloride.

57. DECOMPOSITION OF ZIRCON BY FUSION WITH SODIUM HYDROXIDE

A flow sheet of the decomposition of zircon by fusion with sodium hydroxide is shown in Figure 111.

Fusion. The fusion of zircon with sodium hydroxide yields sodium zirconates and silicates:

$$ZrSiO_4 + 4NaOH = Na_2ZrO_3 + NaSiO_3 + 2H_2O.$$

Other products which are most probably formed are the orthozirconate Na_4ZrO_4, complex zirconosilicates (such as Na_2ZrSiO_5), and other sodium silicates, e. g., $Na_2Si_2O_5$, $Na_6Si_2O_7$.

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Titanium present as an impurity (in the form of rutile and ilmenite) reacts with sodium hydroxide to yield sodium titanates.

Iron and aluminum are present in the melt as ferrite ($Na_2O \cdot Fe_2O_3$) and aluminate ($Na_2O \cdot Al_2O_3$).

The fusion with sodium hydroxide is carried out in iron crucibles or cast iron vessels at 600 to 650°.

The sodium hydroxide is added in a 50% excess (over the stoichiometric amount needed) in order to ensure quantitative decomposition of the zircon. The melt is granulated by pouring into water a thin jet.

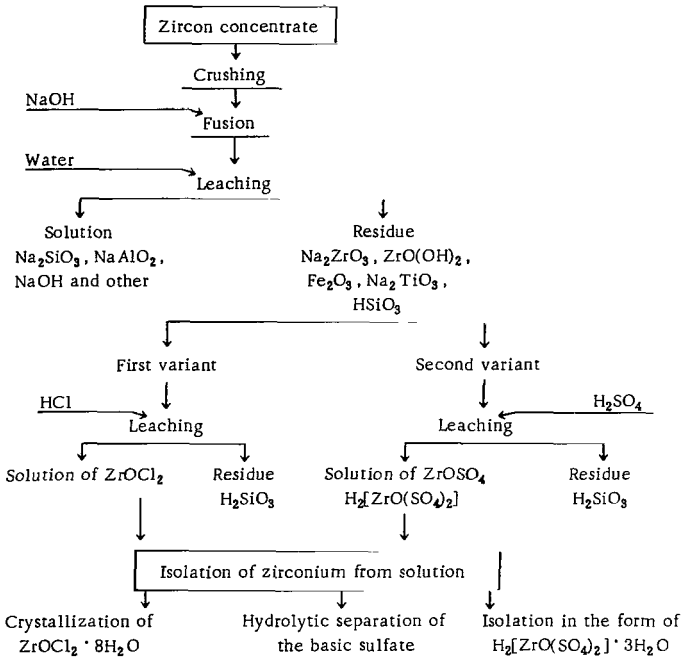

FIGURE 111. Flow sheet of the processing of zircon by fusion with sodium hydroxide.

During the fusion or leaching measures must be taken to prevent spattering of the alkaline melt or of solutions. An exhaust hood must be fitted over the vessel (or crucible) in which the fusion is carried out. An "alkaline mist" (consisting of a stable sodium hydroxide aerosol) which affects the integument and the respiratory system is formed in poorly ventilated rooms. This is difficult if fusion processes have to be carried out on a large scale. The rapid corrosion of steel or cast iron vessels by the alkaline melt is another disadvantage of the process. The fusion with sodium hydroxide has the advantages of requiring a relatively low temperature and of having a high output rate.

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Leaching the melt with water. The leaching of the alkaline melt with water is carried out in iron tanks fitted with stirrers or in drum-type leaching equipment of the ball type, in two stages with intermediate decantation.

During the leaching with water most of the silicon passes into solution in the form of sodium silicate Na_2SiO_3. At the same time there is a partial hydrolysis of sodium zirconate with the formation of zirconium hydroxide:

$$Na_2ZrO_3 + 3H_2O = Zr(OH)_4 + 2NaOH.$$

In the second stage leaching of the residue with water, partial hydrolysis of sodium silicate also takes place as the alkalinity of the solution decreases:

$$Na_2SiO_3 + 2H_2O = H_2SiO_3 + 2NaOH.$$

Sodium titanate remains in the residue together with the zirconium while sodium aluminate passes into solution. The ferrite is decomposed as follows:

$$Na_2O \cdot Fe_2O_3 + H_2O = Fe_2O_3 + 2NaOH.$$

Thus, the residue from the leaching of the melt with water contains sodium zirconate, zirconium hydroxide, residual sodium silicate, silicic acid, sodium titanate, iron oxides, and a certain amount of sodium zirconosilicate. The approximate composition of the residue is: 80 to 84% ZrO_2, 8 to 12% SiO_2, 4 to 6% Na_2O. The residue is forwarded to acid leaching.

Acid leaching. Either hydrochloric or sulfuric acid is used for the leaching. Zirconyl chloride solutions are formed in the former case, while solutions containing zirconyl sulfate and zirconylsulfuric acid are formed in the latter case:

$$Na_2ZrO_3 + 4HCl = ZrOCl_2 + 2NaCl + 2H_2O,$$
$$Na_2ZrO_3 + 2H_2SO_4 = ZrOSO_4 + Na_2SO_4 + 2H_2O,$$
$$ZrOSO_4 + H_2SO_4 = H_2[ZrO(SO_4)_2].$$

Compounds of iron and other elements pass into solution.

A part of the silicic acid remains in the insoluble residue together with the undecomposed zircon, while another fraction is solubilized as a colloid. Coagulants (e.g., carpenter's glue) are added to the solution to coagulate the silicic acid. The voluminous silicic acid precipitate entrains a part of the zirconium.

The dissolution in hydrochloric acid is carried out in heated earthenware or rubber-lined iron tanks fitted with stirrers. Tanks made of a synthetic resin — faolite — may also be used. The dissolution in sulfuric acid is carried out in lead-lined tanks or in tanks lined with acid-resistant ceramic tiles.

The selection of the acid to be used for leaching depends on the required purity of the final product — zirconium dioxide (see below). The solution is separated from the residue (consisting mainly of silicic acid and the undecomposed mineral) and zirconium compounds are precipitated from the solution (see Section 59).

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58. DECOMPOSITION OF ZIRCON BY FUSION WITH LIME

Heating zircon with lime leads to the formation of calcium zirconate and silicates in accordance with the equations:

$$ZrSiO_4 + 2CaO = CaZrO_3 + CaSiO_3; \quad (1)$$
$$ZrSiO_4 + 3CaO = CaZrO_3 + Ca_2SiO_4. \quad (2)$$

Dicalcium silicate Ca_2SiO_4 is preferentially formed under the conditions used in the process. Unlike zircon, calcium zirconate is readily decomposed by acids and zirconium may thus be solubilized. The flow sheet of the process is shown in Figure 112.

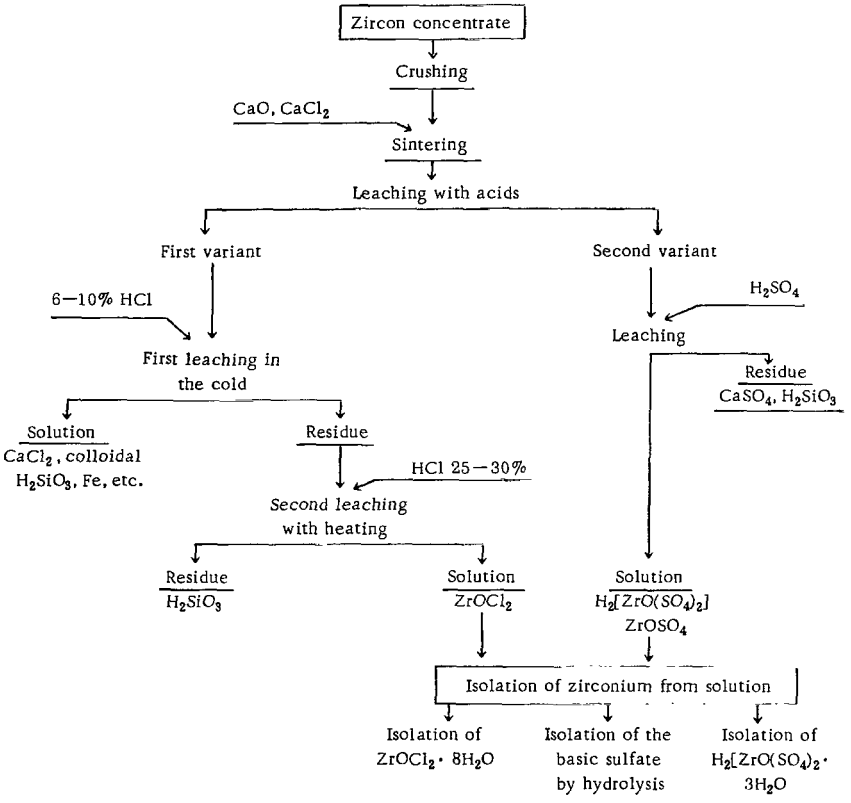

FIGURE 112. Flow sheet of the processing of zircon by sintering with lime.

Sintering with lime. Zircon and lime interact at a noticeable rate only at 1400 to 1500°. However, the addition of alkali-metal and alkaline-earth chlorides (in particular calcium chloride) reduces the process temperature to 1000 to 1100°. The accelerated rate of the reaction in the presence of chlorides is attributed to the formation of an intermediate liquid phase ($CaCl_2$ melts at 774°) which dissolves some of the calcium

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oxide. In addition, it is possible that the reaction is catalytically accelerated because of the chlorinating action of calcium chloride:

$$2CaCl_2 + ZrSiO_4 = ZrCl_4 + Ca_2SiO_4;$$
$$ZrCl_4 + 3CaO = CaZrO_3 + 2CaCl_2.$$

During the sintering the iron oxides react with lime to form calcium ferrite $Ca(FeO_2)_2$; ilmenite reacts to form calcium titanate.

Chalk may be used instead of lime when the reaction rate is somewhat lower.

The amount of the lime or chalk added is 100 to 150% of the stoichiometric (for reaction (2)), while the amount of $CaCl_2$ is about 1/5 (by weight) of the amount of lime added to the charge. The sintering is carried out on the sole of a muffle furnace or in a rotary furnace at 1000 to 1100°. The sintering time is 8 to 10 hours. Under these conditions the degree of decomposition reaches 90 to 94%.

The decomposition of zircon concentrates by sintering with lime and calcium chloride has the following advantages over the fusion with sodium hydroxide: the reagents used are much cheaper and large-scale industrial processing is simpler since rotary furnaces may be used. Hydrochloric or sulfuric acids are used to leach the sintered mass.

Leaching with hydrochloric acid. The sintered mass is first treated with 5 to 10% HCl in the cold. This results in the dissolution of the excess calcium oxide and calcium chloride but calcium zirconate is not affected. Moreover, processing with cold HCl results in the decomposition of most of the calcium orthosilicate. The colloidal silicic acid formed is separated together with the solution. The second leaching is carried out at 85 to 90° with 25 to 30% hydrochloric acid. As a result zirconium is solubilized:

$$CaZrO_3 + 4HCl = ZrOCl_2 + CaCl_2 + 2H_2O.$$

Silicic acid is formed at the same time as a result of the decomposition of residual calcium silicate. A solution of carpenter's glue is used to coagulate the silicic acid. The solution is separated from the residue and zirconium is precipitated by one of the methods described below.

Leaching with sulfuric acid. When the sintered mass is leached with sulfuric acid, calcium remains in the residue as a component of the sulfate. The sintered mass is gradually introduced into concentrated sulfuric acid; the reaction is accompanied by strong heat-up of the mixture, which aids in the separation of the silicic acid (silicic acid is dehydrated upon heating). At the end of the reaction the solution is diluted, filtered, and zirconium isolated.

59. ISOLATION OF ZIRCONIUM FROM HYDROCHLORIC AND SULFURIC ACID SOLUTIONS

At present there are three industrial methods for the isolation of zirconium from hydrochloric and sulfuric acid solutions.

1. Precipitation of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ from hydrochloric acid solutions.

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2. Hydrolytic precipitation of basic zirconium sulfates; this may be carried out from both hydrochloric and sulfuric acid solutions.

3. Isolation of the crystalline zirconylsulfuric acid hydrate $H_2[ZrO(SO_4)_2] \cdot 3H_2O$ from sulfuric acid or zirconium oxychloride solutions.

Isolation of zirconium oxychloride

The method is based on the fact that $ZrOCl_2 \cdot 8H_2O$ is sparingly soluble in concentrated hydrochloric acid while being readily soluble in water and dilute HCl (Figure 113).

The solubility of the oxychloride has a minimum (10.8 g/l) at HCl concentration of 318 g/l; in dilute HCl solutions the solubility is 40 to 50 times higher /7/. In addition, the solubility of $ZrOCl_2$ strongly depends on the temperature (its solubility in concentrated HCl at 70° is about five times that at 20°).

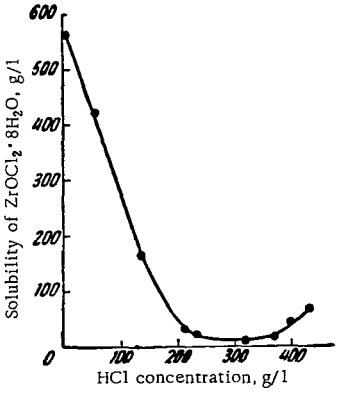

FIGURE 113. Solubility of $ZrOCl_2 \cdot 8H_2O$ in hydrochloric acid at 20°.

Hydrochloric acid is concentrated by evaporation of the solution. During the evaporation the HCl concentration must remain below 20.2% (about 220 g/l) or an azeotropic mixture will be formed*. Even in acid of this concentration the solubility of $ZrOCl_2 \cdot 8H_2O$ is not high ($\sim$ 25 g/l) and, after the solution is cooled, about 70 to 90% of the zirconium initially present in the solution may be isolated as crystals.

The method yields zirconium compounds of a very high degree of purity since most of the impurities (Fe, Al, a part of titanium, and some others) remain in the hydrochloric mother liquor. Also the salt may be purified by recrystallization. Zirconium oxychloride can be readily converted to other pure zirconium compounds: zirconium hydroxide, dioxide, fluorides, nitrate or sulfate. To do this zirconium oxychloride is dissolved in water, zirconium hydroxide precipitated by the addition of ammonia and the hydroxide is then dissolved in the respective acid. Zirconium dioxide prepared by this method contains 99.6 to 99.8% ZrO_2.

Hydrolytic precipitation of basic sulfates

This method is extensively used in industry, as it can be applied to both sulfuric and hydrochloric acid solutions.

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* Azeotropic solutions are solutions which distill without a change in composition (i. e., the liquid and vapor phases have the same composition).

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Isolation from sulfuric acid solutions. In sulfuric acid solutions zirconium is present in the form of zirconyl ions ZrO^{2+} and of complex anions $[ZrO(SO_4)_2]^{2-}$; the ratio of these species is determined by the equilibrium

$$(ZrO)^{2+} + 2(SO_4)^{2-} \rightleftarrows [ZrO(SO_4)_2]^{2-}.$$

The presence of these two ionic species in solution has been confirmed by recent studies carried out with the aid of ion-exchange resins. At sulfuric acid concentrations up to 0.5 to 1.0 N (24 to 50 g/l) zirconium is sorbed on both cation and anion exchange resins. At higher sulfuric acid concentrations adsorption on cation exchange resins ceases, which shows that all the zirconium is in the form of a complex anion. Accordingly, when carrying out the hydrolysis, it is not sufficient to adjust the pH of the solution to that corresponding to the hydrolysis of zirconium sulfate; the worker must also ensure that there is no large excess of SO_4^{2-} ions since the extent of formation of complex ions depends on the sulfate ion concentration in the solution rather than on its acidity. Hydrolytic precipitation of zirconium in fact does not take place when a sulfuric acid solution containing a large excess of the acid is neutralized with soda ash or ammonia. The hydrolysis takes place only if a part of the SO_4^{2-} ions is removed from the solution, e. g., by the addition of $BaCl_2$ or $CaCl_2$ /9/.

When the sulfate-ion concentration in the solution is reduced to a certain minimum (about 0.55 to 0.6 mole/mole ZrO_2), it is possible to achieve nearly quantitative hydrolytic precipitation of basic zirconium sulfate from sulfuric acid solutions as a result of the hydrolysis of zirconyl sulfate. The composition of the precipitated basic sulfates may be described by the general formula $xZrO_2 \cdot ySO_3 \cdot zH_2O$ (the ratio $x:y > 1$). The precipitated basic sulfates have a variable composition, depending on the initial acidity and zirconium content of the solution. The molar ratio $ZrO_2 : SO_3$ in the precipitates ranges from 1 : 0.75 to 1 : 0.2.

The hydrolysis is carried out in dilute solutions with a zirconium content of 40 to 60 g/l, which are neutralized with soda ash to pH $\approx 2-3$. In order to prevent contamination of the precipitates with iron, ferric ions are reduced to ferrous ions with iron turnings (see Section 45).

The solution is heated to 70 to 80° when up to 98% of the zirconium is precipitated as the basic sulfate. The voluminous precipitate of the basic sulfate sorbs iron, aluminum, and other salts present as impurities. The impurities are only partly removed when the precipitates are washed.

Isolation of the basic sulfate from hydrochloric acid solutions. It is much simpler to isolate the basic sulfate from hydrochloric acid than from sulfuric acid solutions since the difficulties associated with the presence of an excess of sulfate ions are absent.

The basic sulfate is precipitated from hydrochloric acid solutions containing 40 to 60 g/l zirconium by the addition of sulfuric acid (about 0.55 mole/mole ZrO_2) followed by neutralization and dilution to a resultant acidity of about 1 to 1.5 gram HCl per liter. The solution is heated to 70 to 80° and the basic sulfate ($ZrO_2 : SO_3$ ratio of about 1 : 0.3) precipitates out. Soluble sulfates (Na_2SO_4, $MgSO_4$) may be added instead of sulfuric acid. The precipitate contains 97 to 98% of the total zirconium.

The basic sulfate precipitates are washed, separated by filtration, dried and ignited (to remove SO_3) at 850 to 900° in muffle furnaces lined with refractories of a high alumina content.

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The method yields technical grade zirconium dioxide containing 97 to 98% ZrO_2. The main impurities are: 0.5 to 1.5% TiO_2, 0.2 to 0.8% SiO_2, 0.1 to 0.15% Fe_2O_3, 0.2 to 0.5% CaO, 0.2 to 0.4% P_2O_5, and up to 0.3% SO_3.

Additional purification of the basic sulfate is required to obtain a product of a higher degree of purity.

Isolation of zirconium as the zirconylsulfuric acid hydrate

The addition of concentrated sulfuric acid to concentrated aqueous solutions of zirconium sulfate or chloride results in the precipitation of crystalline zirconylsulfuric acid hydrate $H_2[ZrO(SO_4)_2] \cdot 3H_2O$.

The dependence of the solubility of the crystalline hydrate on the sulfuric acid concentration is given in Table 39; it will be seen that the solubility in the H_2SO_4 concentration range of 46.7 to 57.4% is very low.

TABLE 39

Solubility of $H_2[ZrO(SO_4)_2] \cdot 3H_2O$ in sulfuric acid solutions at 39.5°C

H_2SO_4 concentration, %	ZrO_2 g/100 g solution	H_2SO_4 concentration, %	ZrO_2 g/100 g solution
31.2	19.50	48.7	0.46
33.1	18.80	51.5	0.33
35.6	16.20	57.4	0.14
39.6	9.60	69.5	0.15
42.5	5.30	70.5	0.50
44.1	3.51	72.9	2.0
46.7	1.03		

The highest degree of separation of the zirconium (94 to 95%) is obtained under the following conditions. One volume of concentrated sulfuric acid is added to two volumes of the sulfate solution containing 120 to 130 g/l zirconium (or to the oxychloride solution containing 200 to 220 g Zr/l). This results in the separation of a white crystalline precipitate which settles rapidly and is separated by filtration through porous earthenware filters.

Further purification is accomplished by dissolving the precipitate in water (one kg of precipitate in one liter of water) and reprecipitating the crystalline hydrate by the addition of concentrated sulfuric acid. This yields a product of a very high degree of purity in which the concentrations of iron, copper, and silver are less than 10^{-5}% each, and the concentrations of calcium, sodium, magnesium, and silicon are below 10^{-3}% each. Pure zirconium dioxide may be produced by igniting the crystalline hydrate of zirconylsulfuric acid at 850 to 900° /8/.

It is advantageous to use the method based on the isolation of zirconylsulfuric acid for the purification of the basic sulfate precipitates prepared by hydrolysis.

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60. PROCESSING OF ZIRCON BY SINTERING WITH POTASSIUM FLUOSILICATE

This method was developed in the USSR by Sazhin and Pepelyaeva /3/. The method is based on the reaction occurring when zircon is heated with potassium fluosilicate:

$$ZrSiO_4 + K_2SiF_6 \rightarrow K_2ZrF_6 + 2SiO_2.$$

The potassium fluozirconate obtained is leached with water and the salt is then crystallized out of solution.

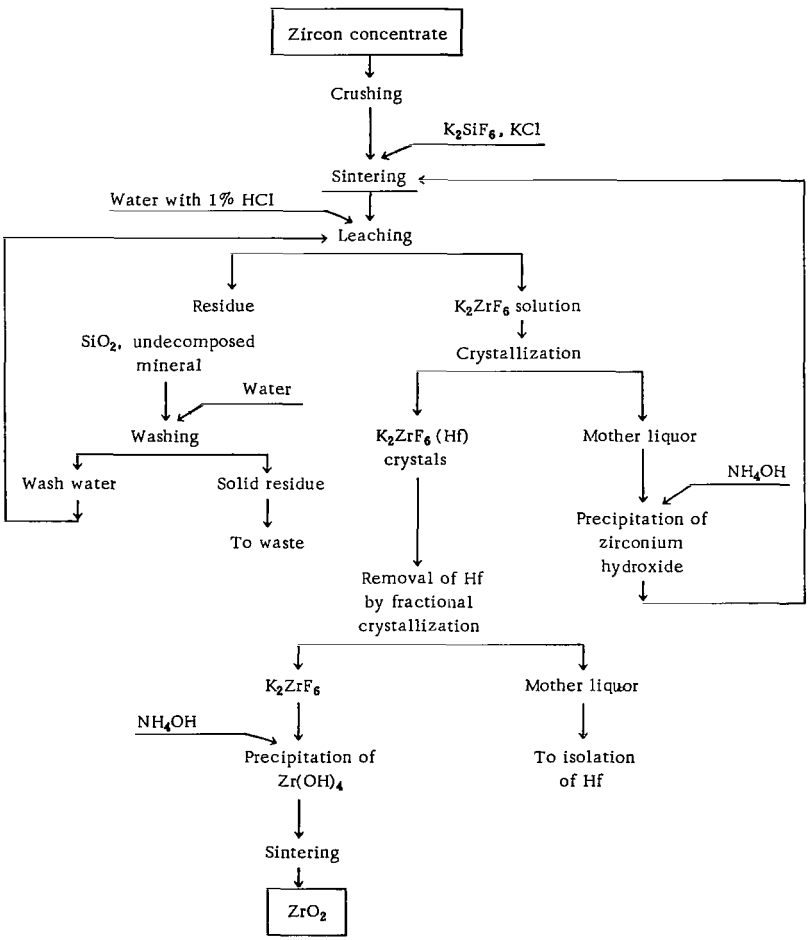

FIGURE 114. Flow sheet of the processing of zircon by fusion with potassium fluosilicate.

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The potassium fluosilicate required for the process is readily prepared from a relatively cheap substance — sodium fluosilicate, which is a by-product of the manufacture of hydrofluoric acid and cryolite. The interaction of a saturated solution of Na_2SiF_6 with a saturated solution of KCl causes precipitation of K_2SiF_6:

$$Na_2SiF_6 + 2KCl \rightarrow K_2SiF_6 + 2NaCl.$$

This can be explained by the fact that the solubility of K_2SiF_6 (~ 1.13 g/l) is much lower than the solubility of Na_2SiF_6 (~ 6.7 g/l).

A flow sheet of the processing of zircon by sintering with potassium fluosilicate is shown in Figure 114. The zircon concentrate is crushed to a particle size of less than 0.074 mm and mixed with potassium fluosilicate and potassium chloride. The potassium chloride intensifies the degree of decomposition of the mineral. The K_2SiF_6 is taken in 50% excess over the stoichiometric amount.

The degree of decomposition of zircon is strongly affected by the sintering temperature of the charge. When the process is carried out at 650 to 700° the degree of decomposition reaches 97 to 98% *. The sintering is carried out in rotary furnaces. The sintered mass consists of burnished and slightly fused grains with a particle size of 0.5 to 10 mm. It is crushed to a particle size of less than 0.15 mm and leached with 1% HCl (at a solid : liquid ratio of 1 : 7) at 85°. The leaching time is 1.5 to 2 hours.

TABLE 40

Solubility of K_2ZrF_6 in water

t, °C	Solubility, g/100 g, H_2O	t, °C	Solubility, g/100 g, H_2O
10	1.22	60	3.81
20	1.55	70	5.06
30	1.92	80	6.90
40	2.37	90	11.11
50	2.94	100	23.53

The mixture is allowed to stand (the temperature of the slurry must not exceed 80°) and the clear solution is forwarded to the crystallization stage. If the solution is filtered, the filtration must be carried out at a high temperature in order to prevent premature crystallization.

The solubility of K_2ZrF_6 increases sharply with increasing temperature (see Table 40). As a result, 75 to 90% of the zirconium present in the solution may be crystallized by cooling the solution (depending on the initial zirconium concentration).

Ammonium hydroxide is added to the mother liquor, and the precipitated zirconium hydroxide is returned to sintering. As impurities accumulate in the mother liquor, they are periodically discarded. The K_2ZrF_6

---

* Because of the difficulties involved in maintaining a constant temperature in rotary furnaces, there are wide fluctuations in the degree of decomposition of the concentrate and it is usually lower than this value.

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crystals prepared by this method from zircon concentrates from the Azov region of the USSR have the following composition: 31.9 to 32% Zr + Hf, 27.2 to 27.6% K, 39.9 to 40.05% F, 0.044 to 0.045% Fe, 0.041 to 0.042% Ti, 0.06 to 0.07% Si, 0.006 to 0.008% Cl, 1.5 to 2.5% Hf (on the zirconium).

Hafnium is separated from zirconium by fractional crystallization.

All leaching and crystallization operations may be carried out in stainless steel equipment; the corrosion of such equipment is negligible because the inner walls are coated with a film of insoluble fluorides.

In order to convert it into zirconium dioxide, potassium fluozirconate is dissolved in water (25 to 30 g K_2ZrF_6 in one liter of water at 50 to 60°) and the resulting solution is poured into a solution of ammonium hydroxide; the NH_4OH is taken in 150% excess over the stoichiometric amount required for the reaction:

$$K_2ZrF_6 + 4NH_4OH = Zr(OH)_4 + 4NH_4F + 2KF.$$

The fluoride salts are removed from the zirconium hydroxide by washing with water containing 0.5% NH_3, the hydroxide is separated by filtration, dried and ignited at 900° to zirconium dioxide.

The precipitation with ammonia frees the zirconium from the iron and titanium which are bound in ammoniacal fluoride complexes and thus only a small fraction is precipitated. Thus, zirconium dioxide containing 0.005% Fe and 0.005% Ti was prepared from fluozirconate containing 0.032% Fe and 0.012 Ti.

This process is characterized by its small number of operations and its simplicity. As will be shown below, hafnium can be readily separated from zirconium by this process, and zirconium dioxide of a high degree of purity can be produced.

61. DECOMPOSITION OF ZIRCON BY REDUCTION WITH CARBON TO CARBIDE OR CARBONITRIDE /1, 2/

Zirconium carbide or carbonitride are produced by reducing the zircon with carbon; during the reduction most of the silicon is removed as SiO whose vapor pressure at 2000 to 2200° is close to one atmosphere.

The main reactions occurring during the reduction of zircon with carbon are:

$$ZrSiO_4 + 6C = ZrC + SiC + 4CO; \quad (1)$$

$$ZrSiO_4 + 5C = ZrC + Si + 4CO; \quad (2)$$

$$ZrSiO_4 + 4C = ZrC + SiO + 3CO; \quad (3)$$

$$ZrSiO_4 + 3C = Zr + SiO + 3CO. \quad (4)$$

In the presence of a suitable amount of carbon in the charge, the reduction occurs mainly in accordance with reaction (3). Silicon monoxide is also formed by a side reaction involving the reduction of zircon by silicon:

$$ZrSiO_4 + Si = ZrO_2 + 2SiO.$$

Moreover, the reduction involves a number of other side reactions, one of which is the formation of the easily melted zirconium silicide $ZrSi_2$.

When using a charge containing 18 to 20% carbon (in the form of powdered coke), 95 to 96% of the silicon is removed as SiO by carrying out the reduction in an electric-arc furnace.

A diagram of one type of one-phase are furnace used for the reductive melting of zircon at one plant in the USA is shown in Figure 115. The furnace bath consists of a steel cylinder 2.14 m in diameter.

The pressed carbon at the bottom serves as one of the electrodes. The second carbon electrode, which is about 600 mm in diameter, is placed in the center of the furnace. A part of the charge adjacent to the walls does not take part in the reaction and serves as a protective thermal insulation layer. Low-voltage

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(~ 50 V) current is supplied to the electrodes and this necessitates the use of a short arc. In such a case the losses of heat through marginal radiation on the walls are minimal. The radiation losses through the cover of the furnace are also very small since the electrode serves as a shield. The total furnace power is 750 kw.

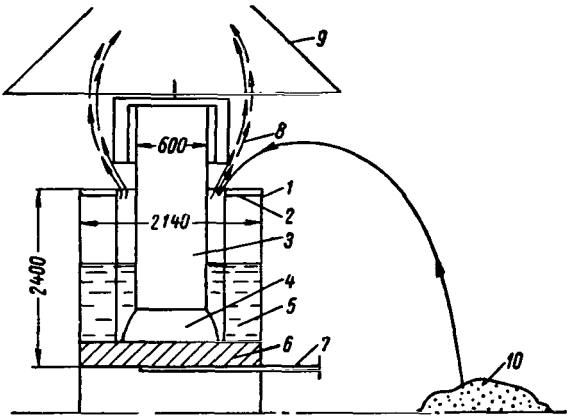

FIGURE 115. Diagram of an arc furnace for the carbidization of zircon.

1—steel jacket; 2—asbestos cover; 3—electrode; 4—fused part of the charge (carbide); 5—charge layer serving as thermal insulator; 6—pressed carbon (lower electrode); 7—current lead to the lower electrode; 8—exhaust gases; 9—exhaust hood; 10—charge.

The furnace is allowed to cool, the mass is discharged by rotating the furnace, and the carbide particles are separated from the fraction of the charge which has not reacted. The consumption of electrical energy is 8000 to 11,000 kwh/ton zirconium carbide.

One of the disadvantages of the process is the fact that the losses caused by dust formation during the charging and discharging of the furnace are high. To reduce dust formation the charge is fed into paper bags. However, even in this case the mechanical losses reach 8%.

Since the pores of the charge contain nitrogen, the product formed in the fusion is usually the carbonitride (a solid solution of zirconium nitride in zirconium carbide). The carbonitride formed has the following approximate composition: 75 to 85% Zr, 3 to 5% C, 2 to 4% Si, up to 2% N, 1 to 2% Fe, up to 2% Ti, and 1 to 10% O.

62. PRODUCTION OF ZIRCONIUM TETRACHLORIDE

Zirconium chloride may be prepared by chlorination of three products: zircon concentrates, zirconium dioxide, and zirconium carbide (or carbonitride).

Chlorination of zircon concentrates

A mixture of zircon concentrate and carbon can be chlorinated at 900 to 1000° at a rate which is sufficiently high to be of practical value. The main

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reaction involved is:

$$ZrSiO_4 + 4Cl_2 + 4C = ZrCl_4 + SiCl_4 + 4CO.$$

A mixture of the pulverized concentrate, carbon and a binder (either coal tar or sulfite-pulping liquors are used as the binder) is pelletized. The pellets are coked at 700 to 800°. The chlorination of the pellets is carried out in shaft furnaces lined with Dinas [silica refractory] bricks. Since the chlorination reaction is endothermic, constant inflow of heat is required to maintain the furnace temperature at 800 to 1000°. The process may be carried out without external supply of heat if a certain amount of air is introduced into the furnace together with the chlorine; the heat evolved in the combustion of a part of the coal in the charge is sufficient to maintain the temperature.

The difference between the volatilization temperature of $ZrCl_4$ (330°) and the boiling point of $SiCl_4$ (58°) permits the condensation of the zirconium chloride in the primary condensers which are maintained at 150 to 180°, and the condensation of liquid silicon chloride in the secondary condensers in which the temperature is maintained at -10° by cooling with water or with a salt solution. The silicon chloride finds use in the production of various organosilicon compounds and may be used as the starting material for the production of semiconductor grade silicon.

Zirconium chloride produced by the above process is contaminated with silica, which is formed as a result of the interaction of a part of the $SiCl_4$ with moisture and oxygen which may be present in the furnace. For the same reason zirconium chloride contains the oxychloride $ZrOCl_2$.

The direct chlorination of zircon in mixture with carbon has recently found increasing industrial use. The disadvantages of the process (the high temperature) are compensated by the elimination of the expenses involved in the pretreatment of the concentrate in order to separate the bulk of the silicon (e. g., by carbidization) and by the production of a valuable by-product — silicon tetrachloride.

Chlorination of zirconium carbonitride /1, 4/

The carbide and carbonitride are chlorinated at a low temperature (350 to 450°) and the heat evolved in the reaction is sufficient to maintain the process even in small chlorinators. The chlorination reactions are:

$$ZrC + 2Cl_2 \rightarrow ZrCl_4 + C + 202 \text{ kcal}$$

$$ZrN + 2Cl_2 \rightarrow ZrCl_4 + \frac{1}{2} N_2 + 160 \text{ kcal}$$

A diagram of a furnace used for the chlorination of zirconium carbonitride in a plant in the USA is shown in Figure 116. The chlorination is carried out in a shaft furnace about one meter in diameter and about 2.5 m high. The chlorine enters the furnace through a perforated graphite plate over which there is a layer of coke particles. The process is started by heating the coke layer with hot air. The carbonitride is then passed over the heated layer and the chlorine is fed to the furnace. Intensive chlorination of the carbonitride starts at 400° and is maintained by the reaction heat evolved.

The condenser is a nickel cylinder 1250 mm in diameter and 2450 mm high. The temperature in the condenser is maintained at 150°. At the exit from the condenser zirconium chloride is screened on a sieve. The screened fraction is degassed in a low vacuum in order to separate $SiCl_4$ and $TiCl_4$. The zirconium tetrachloride produced is contaminated with oxygen and with dust particles entrained from the furnace. The product is bright-yellow.

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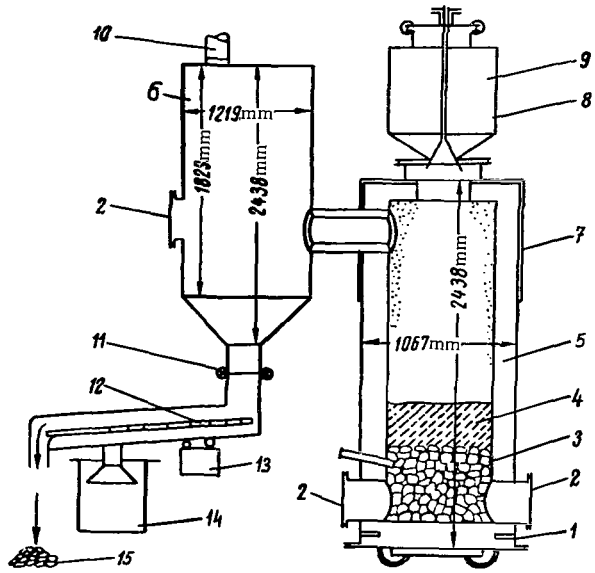

FIGURE 116. Diagram of the apparatus for the chlorination of zirconium carbide.

1—chlorine entry tube; 2—hatch; 3—coke; 4—carbide; 5—Dinas bricks (299 mm); 6—$ZrCl_4$ condenser; 7—expanding coupling; 8—bin (used only during the charging); 9—carbide; 10—exhaust; 11—flexible coupling; 12—sieve; 13—electromagnetic vibrator; 14—fine fraction; 15—coarse fraction.

The cost of zirconium chloride produced by chlorination of zirconium carbonitride is higher than that of the chloride produced by direct chlorination of zircon. The process has the advantages of a low chlorination temperature, simplicity of operation, and the production of technical chloride of a higher degree of purity.

Chlorination of zirconium dioxide /1, 4/

Zirconium dioxide is usually chlorinated if it is the end product of the separation of hafnium from zirconium and if in the production of zirconium metal the pure zirconium dioxide has to be converted into the chloride.

The following main reactions are involved in the chlorination of zirconium dioxide in a mixture with carbon:

$$\frac{1}{2}ZrO_2 + C + Cl_2 = \frac{1}{2}ZrCl_4 + CO; \quad (1)$$

$$\frac{1}{2}ZrO_2 + CO + Cl_2 = \frac{1}{2}ZrCl_4 + CO_2; \quad (2)$$

$$\frac{1}{2}ZrO_2 + \frac{1}{2}C + Cl_2 = \frac{1}{2}ZrCl_4 + \frac{1}{2}CO_2. \quad (3)$$

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At temperatures above 700° the chlorination preferentially takes place in accordance with equation (1), which involves the greatest decrease in free energy.

The chlorination is carried out in shaft furnaces charged with the pelletized raw materials. A diagram of one of the furnaces used and the chlorination apparatus is shown in Figure 117. The furnace consists of a steel shell lined with Dinas bricks. The internal dimensions of the shaft are: diameter 650 to 700 mm, height about 2000 mm. The current is supplied to three graphite plates mounted in the furnace lining.

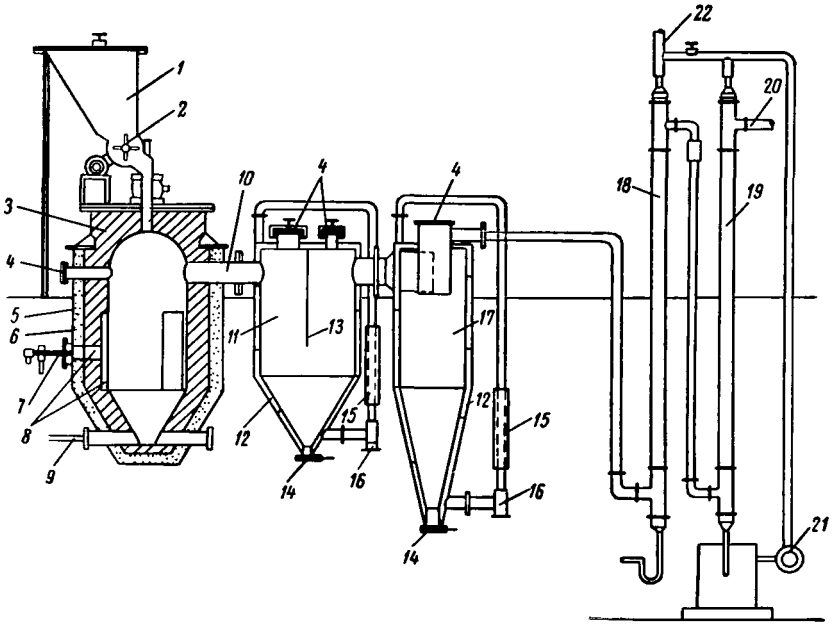

FIGURE 117. Apparatus for the chlorination of a pelletized mixture of zirconium dioxide and carbon.

1—charging bin; 2—feeder; 3—quartz bricks; 4—manholes (for cleaning); 5—steel shell; 6—insulation bricks; 7—cooled copper electrode for the supply of the current; 8—graphite electrode with a sleeve; 9—chlorine supply tubes; 10—gas exhaust (nickel tube); 11—first condenser; 12—air jacket; 13—partition; 14—discharge hole; 15—air heater; 16—fan; 17—cyclone-type condenser; 18—water scrubber; 19—scrubber irrigated with an alkali solution; 20—exhaust tube for the gas (to the cooler); 21—circulation pump; 22—tube for the entry of the wash water.

The charge contains 81% zirconium dioxide, 14.5% gas black and 4.5% dextrin (which acts as a binder). The mixture is moistened with water and pelletized with a roller press (the size of the pellets is 35 × 25 × 20 mm). The pellets are dried at 140°.

When starting the furnace, the pellets are charged to a level somewhat above the middle of the electrodes. Carbon plates are laid over the layer of pellets (from the center to each electrode); the plates are in contact

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with the electrodes and serve for the initial heating of the pellets. An additional amount of the pellets is then fed to the furnace, until the pellets reach the required level. The electrical conductivity of the hot pellets is high enough to permit heating the charge by a direct passage of electric current. The furnace temperature in the vicinity of the heaters is maintained at about 900°, and in the upper zone of the furnace at 250 to 500°. Under normal operating conditions the voltage applied to the electrodes is 15 V and the current is 250 amperes.

The chlorine pipelines, the charging tubes, the gas exhaust lines, and the condensers are made of nickel sheets.

The condensers are fitted with jackets within which there is a circulation of heated air. The temperature of the first condenser is maintained at 150 to 200° and of the second condenser at 100 to 150°. The excess chlorine is absorbed in scrubbers (irrigated with alkaline water) which are fitted after the condensers.

The consumption of electrical energy is 3 kwh/kg of zirconium chloride. The degree of extraction of zirconium into the chloride is 92 to 93%.

Zirconium chloride prepared by one of the above methods contains a number of impurities. The chloride is purified by sublimation (see Section 65).

63. METHODS FOR THE SEPARATION OF HAFNIUM AND ZIRCONIUM

The zirconium used in nuclear power plants must contain less than 0.01% hafnium, whereas zirconium minerals always contain hafnium. The hafnium content of zircon is usually between 0.5 and 2%, but some zircon varieties (e.g., cyrtolite) contain much larger amounts of hafnium. Recently, the production of pure hafnium and hafnium compounds has also attracted interest. Many methods for the separation of these elements have been studied, the most important being:

1) fractional crystallization of the fluoride complexes;
2) fractional distillation (rectification) of the halides and other compounds;
3) extraction with organic solvents;
4) ion-exchange methods;
5) selective reduction of the chlorides.

Fractional crystallization of complex fluorides

The fractional crystallization of the complex fluorides K_2ZrF_6 and K_2HfF_6 has found industrial application in the USSR /3/. The molar solubility of the hafnium salt is about 1.5 times that of the zirconium salt (see Table 41). As a result, fractional crystallization results in the concentration of hafnium (together with the niobium and iron present as contaminants) in the mother liquor.

Studies carried out in the USSR have shown that 16 to 18 successive recrystallizations reduce the hafnium content of K_2ZrF_6 from 2.5% (in % Zr) to a few thousandths of one percent /3/ (Figure 118).

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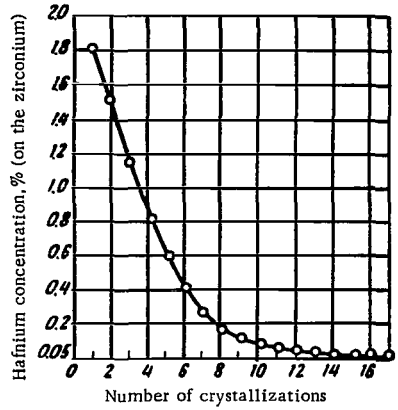

FIGURE 118. Change in the hafnium content of K_2ZrF_6 as a function of the number of successive crystallizations.

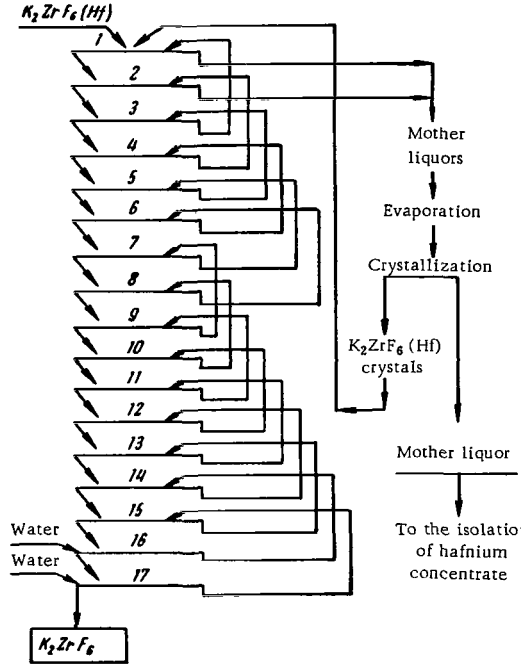

FIGURE 119. Flow sheet of the separation of hafnium from zirconium by fractional crystallization of K_2ZrF_6.

A flow sheet of the fractional crystallization process is shown in Figure 119. The K_2ZrF_6 crystals are dissolved in water at 90° in stainless steel vessels; each fraction of the crystals (except the last two fractions)

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is dissolved in the mother liquor of the preceding crystallization. The solid : liquid ratio during the dissolution is 1 : 7, which corresponds to a K_2ZrF_6 concentration of 0.5 moles/l (or about 140 g/l). The solutions are cooled to 17 to 19°. The solubility of K_2ZrF_6 at that temperature is 16.3 g/l. The crystals formed are allowed to settle, the mother liquor is decanted, the mother liquor from the preceding stage is poured on the crystals and the next crystallization stage performed.

TABLE 41

Solubilities of zirconium- and hafnium-potassium hexafluorides

Solvent	Solubility at 20°, moles/l		Solubility ratio K_2HfF_6/K_2ZrF_6
	K_2ZrF_6	K_2HfF_6	
5.89 M HF	0.1297	0.1942	1.5
0.125 M HF	0.0655	0.1008	1.54
Water	0.0576	—	—

The first and second mother liquors which are most concentrated in hafnium are withdrawn from the crystallization cycle (Figure 119) and evaporated to 1/5 to 1/6 of the initial volume. The K_2ZrF_6 crystals precipitated from the evaporated solution and the hafnium present in the crystals as an impurity are returned to the first crystallization stage, while zirconium hydroxide containing about 6% Hf is precipitated from the mother liquor by the addition of ammonia; the hydroxide is used as the starting compound for the production of pure hafnium.

With the above method, the yield of pure K_2ZrF_6 crystals (with a hafnium content $\sim 0.01\%$) is 80%.

Separation by extraction

Zirconium and hafnium may be separated by selective extraction (from aqueous solutions) with various organic solvents: organophosphorus compounds, ketones, and amines. As an example, we shall consider the extractions with tributyl phosphate and with methyl isobutyl ketone.

The extraction methods are distinguished by their high output; they can be carried out as a continuous process.

Extraction with tributyl phosphate (TBP)*. Tributyl phosphate extracts zirconium and hafnium from solutions containing the oxychlorides or nitrates of these elements. The extraction is carried out most conveniently from nitrate solutions containing free nitric acid.

In the organic phase zirconium and hafnium nitrates are present as complexes with TBP.

The following reaction takes place during the extraction

$$ZrO^{2+} + 2H^+ + 4NO_3^- + 2TBP \rightleftarrows Zr(NO_3)_4 \cdot 2TBP + H_2O.$$

---

* The properties of tributyl phosphate have been described above.

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The equilibrium constant of the reaction is

$$K = \frac{[Zr(NO_3)_4 \cdot 2TBP]}{[ZrO^{2+}][H^+]^2[NO_3^-]^4[TBP]^2}.$$

The ratio

$$\frac{[Zr(NO_3)_4 \cdot 2TBP]}{[ZrO^{2+}]} = \alpha_{Zr},$$

where α is the distribution coefficient.
Hence

$$\alpha_{Zr} = K[H^+]^2[NO_3^-]^4[TBP]^2.$$

This equation shows that the degree of extraction increases with increasing acidity, nitrate ion concentration and TBP concentration.

As is evident from Figure 120, the distribution coefficient of zirconium (α_{Zr}) is higher than that of hafnium at all nitric acid concentrations /10/. The higher extractability of zirconium is due to the lower degree of dissociation of its nitrate. The degree of dissociation of hafnium nitrate decreases sharply with increasing nitric acid concentration. Hence, the separation coefficient $\beta = \frac{\alpha_{Zr}}{\alpha_{Hf}}$ decreases from 12 to 4 as the HNO_3 concentration is increased from 6N to 9N (Figure 120). The extraction should be carried out from solutions containing 5 to 6 N HNO_3 (i. e., at high separation coefficients).

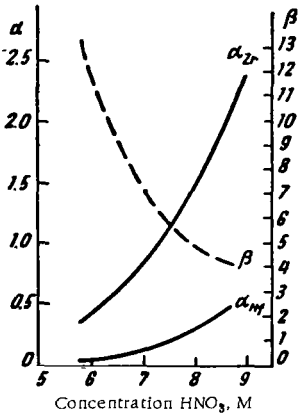

FIGURE 120. Dependence of the distribution and separation coefficients of zirconium and hanfium on the nitric acid concentration.

Since the TBP has a high density and viscosity, it is usually mixed with inert diluents. The extraction is carried out in columns or in extractors of the mixer-settler type (Figures 63 to 66). The extraction in a fourteen-stage extractor of the mixer-settler type is schematically shown in Figure 121. The feed solution containing 125 g/l ZrO_2, 5 M HNO_3 and 2.4% Hf (in % Zr) is introduced at the fifth stage. Here it is combined with the washing solution (5.4 M HNO_3) which is moved from the first stage in countercurrent to the organic solvent, which is introduced at the fourteenth stage. A 40% solution of TBP in n-heptane (C_7H_6) is used as the extractant. The zirconium and the nitric acid are reextracted from the organic phase with water. To recover the nitric acid, the aqueous solution is evaporated to dryness and nitric acid and nitrogen oxide vapors are trapped.

The extraction purifies zirconium not only from hafnium but also from a number of other impurities (Al, Ca, Fe, Mg, Si, Ti).

Extraction with methyl isobutyl ketone (hexone) /20/. Methyl isobutyl ketone is used in industrial practice as an extractant for solutions of

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zirconium and hafnium sulfates or oxychlorides containing ammonium thiocyanate NH_4CNS. The composition of zirconium compounds in such solutions has not been thoroughly studied. It can be expected that in addition to the simple thiocyanates $Me(SCN)_4$ the solutions also contain complex anions such as $[Me(SCN)_6]^{2-}$, (where Me=Zr or Hf).

The organic solvent is preliminarily saturated with thiocyanic acid HCNS. The hafnium is preferentially extracted into the organic phase, and the separation coefficient may be as high as 80.

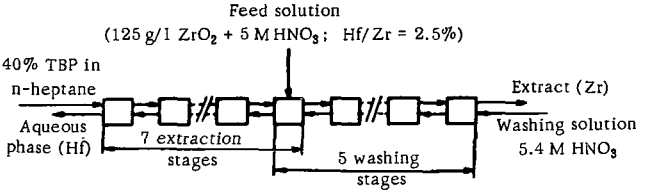

FIGURE 121. Flow sheet of the separation of zirconium and hafnium by continuous extraction. Each square represents one mixer-settler stage.

The aqueous solution (reffinate) containing pure zirconium (the Hf content is 0.005%) is treated with the pure solvent which extracts HCNS. Zirconium is then separated from the solution by one of the methods described above.

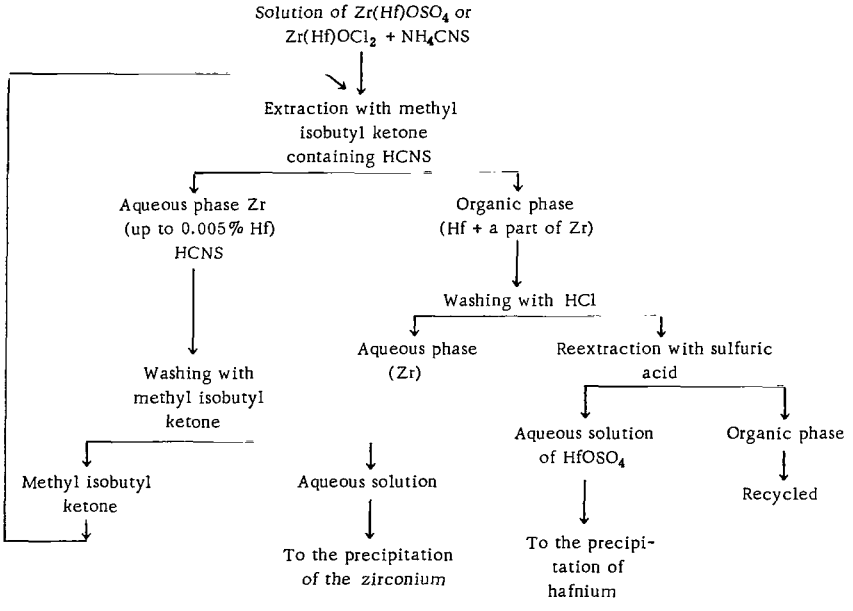

FIGURE 122. Flow sheet of the separation of zirconium and hafnium by extraction with methyl isobutyl ketone from solutions containing thiocyanates.

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The organic phase (extract) containing hafnium and some zirconium is washed with hydrochloric acid to extract the zirconium. The hafnium is then reextracted with a sulfuric acid solution and hafnium compounds are isolated from the solution. A flow sheet of the process is shown in Figure 122.

Ion exchange methods*

Zirconium and hafnium may be separated by ion exchange on cation exchange (when the zirconium and hafnium are present in the solution as cations) or anion exchange resins. The cation exchange separation from nitric acid solutions /10/ will be described as an example.

ZrO^{2+} and HfO^{2+} are first sorbed on the cation exchange resin at the top of the column or in a separate column until it becomes saturated. They are then eluted with 0.5 M H_2SO_4. Zirconium is eluted first and moves to the bottom of the column ahead of the hafnium. With a column of sufficient length this method may be used to extract 95 —98% zirconium with a hafnium content of less than 0.01%.

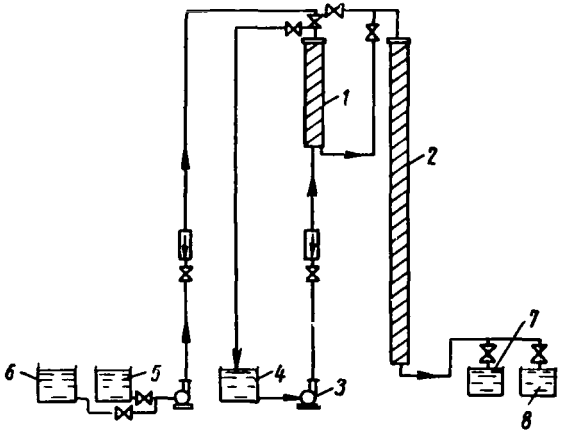

FIGURE 123. Flow sheet of the separation of zirconium and hafnium by ion exchange.

1 —saturation column; 2—column for separation by elution; 3—pump; 4—storage tank for the starting solution containing $Zr(Hf)(NO_3)_2$ + 2 M HNO_3; 5—storage tank containing 0.5M H_2SO_4 used for elution of zirconium; 6—storage tank for 1.5 M H_2SO_4 used for elution of hafnium; 7—collector for solution of pure zirconium in H_2SO_4; 8—collector for the hafnium-containing sulfuric acid solution.

During the elution use is made of the different tendencies of ZrO^{2+} and HfO^{2+} ions to form $[ZrO(SO_4)_2]^{2-}$ and $[HfO(SO_4)_2]^{2-}$ complex ions.

The flow sheet of the process is shown in Figure 123. The solution (17 g/l Zr and 2 M HNO_3) is circulated for a while through the saturation column. A 0.51 M solution of H_2SO_4 is then passed first through the saturation column and then through the separatory column (which is packed with cation-exchange resin in the H-form) until hafnium appears in the solution at the exit of the column. The filtrate, which is collected, contains zirconium.

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* The principle of the ion exchange methods for the separation of elements with similar properties has been discussed in Chapter VI.

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The elution is then continued with 1.5 M H_2SO_4 to extract the fraction containing the hafnium and the remaining fraction of the zirconium. This method may be used to recover 93% of the zirconium with a Hf content of 0.035%.

The drawback of the ion exchange method is its low output (about 0.05 g Zr/hr per cm^2 of column cross section). It gives, however, a sharp separation and may be used as a continuous method.

Rectification

This method of separation is based on the differences between the boiling points of some zirconium and hafnium compounds — chlorides, complexes of Zr and Hf chlorides with phosphorus oxychloride, and alcoholates. The rectification of chlorides is the most important since the separation yields the pure chlorides $ZrCl_4$ and $HfCl_4$ which may be used directly for the production of the metals.

The process is complicated by the fact that at atmospheric pressure the zirconium and hafnium chlorides undergo sublimation at temperatures below their melting points. They can be melted only under the pressure of their own vapor. Thus, $ZrCl_4$ melts at 437° under 18.7 atm. At that temperature the vapor pressure of hafnium chloride is 31.8 atm. The ratio of these pressures (i.e., 1.7) is the separation coefficient for one rectification stage. These data show that zirconium and hafnium can be separated by rectification, but the rectification must be carried out under pressure in order to have chloride vapors in equilibrium with the liquid phase. Research is being carried out in this direction, and columns for rectification under pressure are being developed.

The rectification of "complex chlorides", i.e., substances of the general formula $3MeCl_4 \cdot 2POCl_3$ (where *Me* is Zr or Hf), has been studied more thoroughly and has been used on a pilot-plant scale.

Recent studies have shown that these "complex chlorides" are not separate species but azeotropic mixtures /11/. They are readily prepared by heating ZrO_2 with phosphorus pentachloride or by the reaction of the chloride with phosphorus oxychloride:

$$3ZrCl_4 + 2POCl_3 = 3ZrCl_4 \cdot 2POCl_3,$$
$$3ZrO_2 + 6PCl_5 = 3ZrCl_4 \cdot 2POCl_3 + 4POCl_3.$$

The "complex chlorides" have low boiling points (the bp of Zr salt is 100°) and their boiling points differ by 5°. The boiling point of $3ZrCl_4 \cdot 2POCl_3$ is 360 ± 1° and that of $3HfCl_4 \cdot 2POCl_3$ is 355 ± 1°.

According to different authors, the separation coefficient for the above two compounds is 1.14 to 1.16.

Successful rectification may be carried out in sieve-tray glass columns and in nickel columns. A single rectification in a column with 50 trays yielded a zirconium fraction containing < 0.005% Hf (the initial Hf concentration was 1%). The yield of zirconium was 40%.

Although the rectification of the complex chlorides is highly effective, it has the disadvantage of yielding a final product which cannnot be used directly for the production of the metal. A multistage processing method must be employed. The complex chloride is decomposed with an alkali solution to separate the phosphorus (which is dissolved as the phosphate Na_2HPO_4) and to prepare ZrO_2. The ZrO_2 is then chlorinated to yield $ZrCl_4$.

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There is a simpler method in which the complex chloride is fused with NaCl and is then subjected to thermal decomposition yielding sodium chlorozirconate /21/:

$$3ZrCl_4 \cdot 2POCl_3 + 6NaCl \xrightarrow{300-400^\circ C} 3Na_2ZrCl_6 + 2POCl_3\uparrow;$$
$$Na_2ZrCl_6 \xrightarrow{800^\circ C} 2NaCl + ZrCl_4\uparrow.$$

In this case zirconium chloride is obtained directly.

In another method, the complex chloride vapor is passed through a layer of coke heated to 800°. The following reaction takes place:

$$3ZrCl_4 \cdot 2POCl_3 + 2C \xrightarrow{800^\circ C} 3ZrCl_4 + 2PCl_3 + 2CO\uparrow.$$

Phosphorus trichloride (bp 75°) can be easily separated from $ZrCl_4$ /21/.

Selective reduction of chlorides

Zirconium chloride is reduced more readily than hafnium chloride. Thus, at 400 to 450° $ZrCl_4$ is reduced by zirconium powder to the non-volatile chlorides $ZrCl_3$ and $ZrCl_2$.

The reduction of $ZrCl_4$ (containing 1.5% Hf) by zirconium powder, at 420°, yields a sublimate containing 30% Hf; the yield of Hf is up to 95%. The reduction product is a mixture of $ZrCl_3$, $ZrCl_2$ and the excess zirconium powder; its hafnium content is reduced to 0.05 to 0.1%.

Hafnium-free zirconium may be isolated from the reduction product by heating in vacuo; this causes decomposition of the lower chloride by the reactions:

$$2ZrCl_3 \rightarrow ZrCl_2 + ZrCl_4$$

and

$$2ZrCl_2 \rightarrow Zr + ZrCl_4.$$

Hafnium-free zirconium chloride is distilled off in the process. The residue containing the $ZrCl_2$ and the zirconium contaminated with hafnium is returned to the reduction stage. The hafnium-rich sublimate (up to 30% Hf) may be processed by the extraction and ion exchange methods described above.

Aluminum may be used instead of zirconium powder as the reducing agent. Quantitative reduction may then be carried out at temperatures as low as 300°. The hafnium-rich sublimate is contaminated with large amounts of aluminum chloride, but its separation is not difficult.

The selective reduction method is characterized by a high effectiveness and can be readily combined with the subsequent processes for the conversion of chlorides to the metals.

64. MANUFACTURE OF ZIRCONIUM

The technological problems accompanying the production of ductile zirconium are similar to those involved in the production of metallic titanium, which were discussed above.

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Like titanium, zirconium actively absorbs oxygen, nitrogen, and hydrogen. The solubility of oxygen in zirconium reaches 40 at.% (10.6% by weight). Zirconium containing more than 0.2% oxygen cannot be mechanically worked. The solubility of nitrogen in zirconium is about 20 at.%. The mechanical properties and corrosion resistance of pure zirconium are strongly affected by its nitrogen content. The solubility of hydrogen in α-zirconium is up to 5 at.%, and in β-zirconium it is higher. The presence of hydrogen in zirconium (even at concentrations of 0.003%) markedly reduces the impact strength of the metal. Carbon, CO, and CO_2 react with zirconium at high temperatures, yielding the refractory carbide ZrC (mp 3530°). The presence of carbon has little effect on the mechanical properties of zirconium but reduces its corrosion resistance to water at high temperatures.

In parallel with the similarity of their properties, there is a noticeable similarity in the methods of production of zirconium and titanium. These methods shall accordingly be discussed more briefly. They may be classified into three groups:

1. Thermal reduction with metals:
   a) reduction of zirconium tetrachloride by magnesium;
   b) reduction of potassium fluozirconate K_2ZrF_6 by sodium and of zirconium fluoride by calcium;
   c) reduction of zirconium dioxide by calcium or calcium hydride.
2. Electrolysis of molten salts.
3. Thermal dissociation of zirconium iodide.

The main commercial method for the production of ductile zirconium is based on the reduction of $ZrCl_4$ with magnesium. Zirconium powder (which is used as such) is produced by reduction of K_2ZrF_6 by sodium and by reduction of ZrO_2 by calcium or calcium hydride. Electrolytic methods for the production of zirconium have been increasingly used.

Thermal dissociation of zirconium iodide is used for the production of zirconium of the utmost purity. When necessary, the method is used for the refining of zirconium sponge or powder.

The strength of pure zirconium is not high enough and its corrosion resistance is markedly affected by the presence of very small amounts of certain contaminants (e.g., nitrogen). The mechanical properties and the corrosion resistance are improved by the addition of alloying elements.

65. THERMAL REDUCTION OF ZIRCONIUM CHLORIDE WITH MAGNESIUM /1, 4, 12, 20/

The reduction of zirconium chloride by magnesium is carried out by the Kroll process (similar to the reduction of titanium chloride by magnesium) and is based on the interaction of $ZrCl_4$ vapor with liquid magnesium:

$$ZrCl_4(gas) + 2Mg(liquid) \rightarrow Zr(solid) + 2MgCl_2(liquid) + 52.5\,kcal.$$

The crude zirconium chloride, which is prepared by one of the above described methods (see Section 62), is purified by sublimation in a separate vessel (the separate process) or in the apparatus used for the reduction (the combined process).

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The separate process

Purification of zirconium tetrachloride by sublimation. Zirconium tetrachloride is usually contaminated with the oxychloride $ZrOCl_2$, with 1 to 2% iron (as $FeCl_3$), occasionally with chromium (as $CrCl_3$), and very small amounts of titanium and silicon. In addition it may contain (as a mechanical contaminant) particles entrained from the furnace during the chlorination.

In order to remove iron and chromium, $FeCl_3$ and $CrCl_3$ are preliminarily reduced by hydrogen (at 200 to 300°) to $FeCl_2$ and $CrCl_2$. The lower chlorides have high boiling points ($FeCl_2$ 1030°, $CrCl_2$ 1300°) and are not volatilized at the sublimation temperature of $ZrCl_4$ (450 to 660°). $ZrOCl_2$ is also not volatilized under these conditions.

A diagram of the apparatus used for the purification of zirconium chloride is shown in Figure 124. A crucible (made of a Ni-Cr alloy*) containing crude zirconium chloride is placed in a stainless steel retort. In order to create a larger volatilization surface the chloride is distributed on trays placed one over the other. The retort is covered with a hermetically sealed lid made of lead-antimony eutectic (mp 247°). This alloy may be either cooled until solid (in order to maintain a gas-impermeable seal) or maintained in the molten state when the lid serves as a safety valve.

A coil-shaped, air- or water-cooled chloride condenser, which is introduced into the retort, is fastened to the lid. The retort is placed in a furnace with three temperature zones. The alloy is frozen by cooling, the vessel is evacuated and then filled with hydrogen (these operations are repeated twice) and the reduction of iron chloride is carried out in the lower part of the retort at 200 to 300°. The HCl vapor formed is then evacuated together with the hydrogen. The reduction is repeated, the alloy in the hydraulic seal is melted and the chloride is sublimed by gradually increasing the temperature in the lower part of the retort from 400 to 650°.

The temperature of the upper part of the retort and the lid is maintained at 400° (above the sublimation temperature of $ZrCl_4$) in order to ensure that the chloride condenses only on the coil, which is cooled first with air and then with water.

The sublimation in the reactor 700 mm in diameter and 1750 mm high continues for about 30 hours. The sublimation yields about 200 kg of purified chloride. The iron content in the purified product is reduced to 0.1%, and the iron is present as $FeCl_2$. Additional amounts of iron are subsequently removed in the reduction of the chloride vapor to the metal. The yield of the sublimed chloride depends on the purity of the starting chloride (mainly on the $ZrOCl_2$ content) and ranges from 90 to 96%.

The apparatus is cooled and the lid with the chloride condensate is transferred to the apparatus for thermal reduction by magnesium. The density of the condensate on the coil is about 2.2 to 2.3 g/cm^3.

Reduction. The reduction is carried out in an apparatus resembling the sublimation vessel (Figure 125). A steel crucible containing the required amount of magnesium bars (a 20% excess of magnesium is taken)

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* The alloys used in Inconel X, with the composition: 72.7% Ni, 15% Cr, 7% Fe, 1% Nb, 2.5% Ti, 0.7% Al, 0.7% Mn, 0.4% Si, and 0.05% C.

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is placed on the floor of the vessel. The converter with sublimed zirconium chloride is placed in the upper part of the vessel. The lid is sealed in the same way as in the sublimation apparatus. A drip pan and shields are fitted over the crucible to prevent radiation heat transfer and the penetration of solid zirconium chloride particles into the crucible.

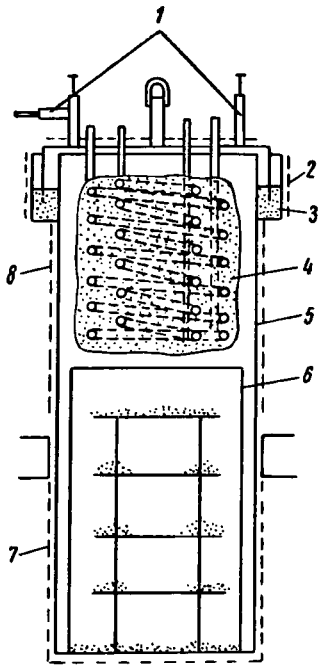

FIGURE 124. Diagram of vessel used for the purification of $ZrCl_4$ by sublimation.

1—valves for the supply of hydrogen and the evacuation and removal of gases; 2—heater of the hydraulic seal; 3—hydraulic seal (Pb-Sb alloy); 4—coil (condenser); 5—retort; 6—crucible containing crude $ZrCl_4$; 7 and 8—heaters.

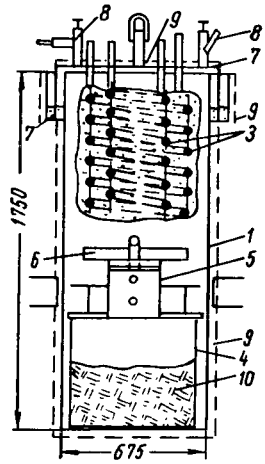

FIGURE 125. Diagram of vessel used for the reduction of $ZrCl_4$ by magnesium.

1—retort; 2—hydraulic seal; 3—condenser with the sublimed chloride; 4—crucible; 5 and 6—shields; 7—lid; 8—valves; 9—heaters; 10—reaction mixture.

The apparatus has three heating zones: the lower zone containing the crucible, the intermediate zone containing the chloride, and the upper zone, which serves for the heating of the ring-shaped groove and the lid.

Before the beginning of the reduction the apparatus is evacuated and filled with argon (the evacuation and filling is repeated in order to ensure complete removal of air). The lower zone is then heated to 825°, i. e.,

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to a temperature above the melting point of $MgCl_2$ which is formed in the reduction process. At the same time the intermediate zone of the retort is heated to 450 to 500°, i. e., to the temperature required for the volatilization of zirconium chloride. At the end of the reduction the temperature of the intermediate zone is increased to 650°. The reaction of the gaseous $ZrCl_4$ with the liquid magnesium results in a continuous removal of chloride from the gaseous phase and thus in the volatilization of further amounts of chloride from the coil.

The presence of an inert gas in the retort reduces the volatilization rate of the chloride and thus reduces the reduction rate. Rapid volatilization takes place in the absence of an inert gas, and the reaction is so fast that the reaction mass may be overheated and the crucible melted. This is due to the fact that the reduction is exothermic. The pressure, which may increase as a result of the overheating of the reaction mass during the reduction is automatically decreased by maintaining the Pb-Sb alloy in a molten state (at 250 to 300°).

Two hundred kg of $ZrCl_4$ are reduced in one operation in a vessel 700 mm in diameter and 1750 mm high, yielding about 75 kg of zirconium. The duration of the process is 24 to 30 hours. The zirconium yield is $\sim$ 93 %.

The container is cooled to room temperature and the crucible is taken out. The zirconium is at the bottom of the crucible in the form of a sponge. It is protected against oxidation by a dense layer of magnesium chloride.

The combined process

The vessel used for the combined sublimation of the chloride and its subsequent reduction with magnesium is shown in Figure 126. Its use eliminates the transfer of the sublimed $ZrCl_4$ from one vessel to another, which brings the chloride into contact with air and causes its partial hydrolysis. Moreover, carrying out both processes in a single vessel reduces the total process time by about 35 %.

In the combined vessel (Figure 126) a container with zirconium chloride is fitted over the crucible containing the magnesium bars.

The vessel is covered with a lid fitted with a coil. It is sealed with the aid of a Pb-Sb alloy seal, as described above. At first the vessel is evacuated, filled with hydrogen and the iron and chromium chlorides are reduced at 300°. It is evacuated to remove the HCl vapors, then filled with argon and the reduction is carried out. The lower zone of the apparatus is heated to 825°, which also causes an increase in the temperature of the intermediate zone (to about 400 to 450°). The $ZrCl_4$ is volatilized and reacts with the molten magnesium.

When the apparatus is charged with 250 kg of $ZrCl_4$, the reduction time is about 15 hours. The temperature of the intermediate zone is then increased to 650° in order to volatilize the remaining $ZrCl_4$ which condenses on the water-cooled coil. The total process cycle has a duration of 44 hours, as compared with about 64 hours in the separate process.

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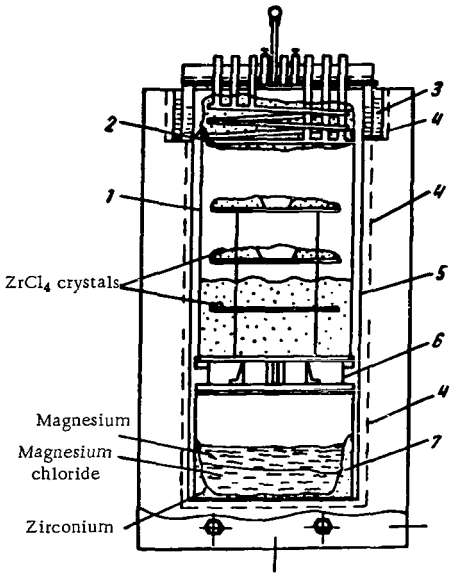

FIGURE 126. Diagram of apparatus for the combined purification of $ZrCl_4$ by sublimation and reduction of vapor with magnesium.

1—crucible with crude $ZrCl_4$; 2—coil condenser; 3—hydraulic seal (Pb-Sb alloy); 4—heaters; 5—retort; 6—shields; 7—crucible with magnesium.

The vacuum-thermal distillation of magnesium and magnesium chloride

Magnesium and magnesium chloride are separated from zirconium by vacuum distillation at 900 to 920°, as in the case of titanium. A diagram of the vacuum-thermal distillation apparatus is shown in Figure 127.

The crucible used for the reduction, together with the reaction mixture, is placed upside down in the retort. The retort is evacuated to 10^{-4} to 10^{-5} mm Hg and the crucible is heated to 825°; as a result the bulk of the magnesium chloride descends through a funnel into a ring-shaped stainless-steel container placed below the crucible. The remaining magnesium and chloride are distilled and condense in the lower, cooled part of the retort.

The upper part of the retort which contains the crucible is heated with the aid of a lifting electrical furnace. The space between the retort and the furnace is evacuated in order to prevent bending of retort walls under the atmospheric pressure. The removal of magnesium and magnesium chloride is accompanied by the removal of the hydrogen absorbed by the zirconium.

The duration of the distillation is 12 to 16 hours. The retort is cooled for a long time in vacuo. In order to accelerate the cooling of the retort

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the vacuum furnace is raised when the temperature of the upper part drops to 400°.

Various types of sponge are formed in the crucible after the distillation. The bulk (70%) consists of a dense metal containing almost no magnesium or magnesium chloride.

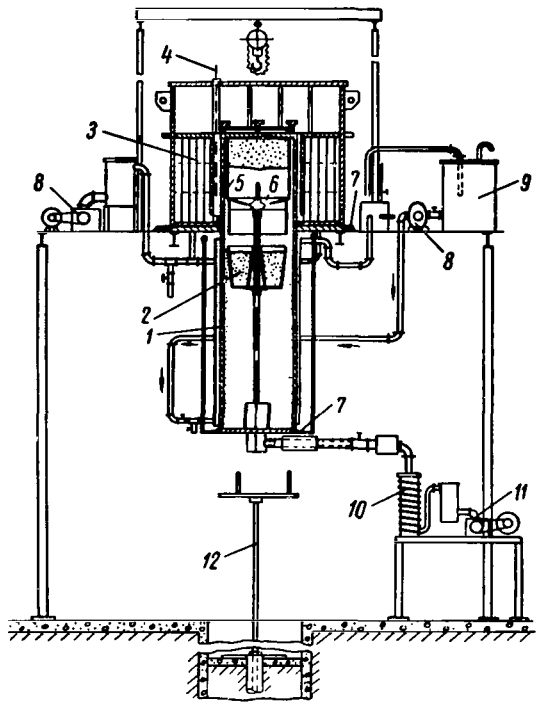

FIGURE 127. Diagram of installation for the vacuum-thermal purification of zirconium sponge.

1—retort; 2—collector for molten $MgCl_2$; 3—lifting electrical furnace; 4—thermocouple; 5—crucible containing the sponge; 6—funnel; 7—rubber gaskets (water-cooled vacuum seals); 8—oil-cooling system for the lower part of the retort; 9—water-circulation heat exchanger for the cooling of oil; 10—diffusion pump; preliminary vacuum pump; 12—lifting device.

The sponge is extracted from the crucible by means of a pneumatic rack press or a chisel in an argon atmosphere and is ground in a conical crusher to a particle size of about 6 mm. The large particles are crushed with the aid of a 200 ton press. Uniform 100 kg batches of sponge are prepared by mixing various types of sponge in mixers.

The approximate impurities content (in % by weight) of the zirconium sponge is:

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Al	0.003	Cu	0.003	Ni	<0.0002
B	$<2 \cdot 10^{-5}$	Fe	0.065	O	0.06—0.1
C	0.0095	Hf	0.0085	Pb	0.007
Cd	<0.002	Mg	0.01	Si	0.002
Co	<0.0002	Mn	0.002	Ti	<0.005
Cr	0.0015	N	0.004	V	<0.001

66. REDUCTION OF POTASSIUM FLUOZIRCONATE BY SODIUM

The complex fluoride K_2ZrF_6 is reduced by sodium if the metal powder produced need not be of a high degree of purity (e.g., for use in pyrotechnics or in electronics).

As compared with the reduction of zirconium chloride, the reduction of potassium fluozirconate has the advantages of being a simple production technique and of being convenient in handling since the salt is not hygroscopic and is stable in the air.

The reduction is carried out with metallic sodium since the sodium fluoride formed in the reaction can be readily leached with water out of the bulk of the zirconium. The reduction is based on the reaction:

$$K_2ZrF_6 + 4Na = Zr + 4NaF + 2KF.$$

The heat of reaction is about 264 kcal/kg charge (K_2ZrF_6 + 4Na). The heat of reaction does not suffice to support a spontaneous reaction and external heating is required.

The reduction may be carried out in hermetically sealed steel reactors of the "bomb" type, which are heated to 800 to 900°. After cooling the solidified mass is taken out of the crucible by crushing with a pneumatic hammer. In order to separate the salts from the powder, the mass is ground in a wet mill and leached with water in tanks fitted with stirrers. Since the reaction mass contains an excess of sodium which reacts vigorously with water, the material is gradually introduced into the water in small portions.

In order to leach out the iron, the material is treated with dilute hydrochloric acid, rinsed with water, separated by filtration and dried at 60°. The drying must be carried out with caution since the material has a tendency to burst into flame spontaneously.

67. REDUCTION OF ZIRCONIUM DIOXIDE BY CALCIUM AND CALCIUM HYDRIDE

Zirconium dioxide is reduced by calcium or calcium hydride under conditions resembling those used for titanium (see above).

Even in the presence of a large excess of calcium (50 to 100%) and even if the reaction is carried out in hermetically sealed apparatus, the powder obtained after leaching the calcium oxide contains 0.3 to 1% oxygen and 0.03 to 1% nitrogen. When the reduction is carried out in a purified argon atmosphere, the nitrogen content depends on the nitrogen content

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of the calcium. The powders produced are suitable for use in vacuum technology, pyrotechnics, photographic flash powders and for military uses.

The reduction may be carried out in hermetically sealed reactors; when using small size reactors, the lid is welded before each reduction. The reaction is conducted at 950 to 1100°. The calcium oxide is leached with dilute hydrochloric acid. The oxygen content is reduced by holding the zirconium powder in a molten calcium bath or in calcium vapor; the use of calcium vapor is more effective.

The difficulties experienced in freeing the zirconium from oxygen are due to the fact that the oxygen is in the form of a solid solution.

The reduction by calcium hydride is carried out at approximately the same temperatures as those used in the reduction with calcium (900 to 1100°); the product is zirconium hydride, which is used for the production of zirconium articles by powder metallurgy techniques.

68. PRODUCTION OF ZIRCONIUM BY ELECTROLYSIS

Many workers found that zirconium may be produced by electrolytic reduction of its halides in molten salts.

The best results were obtained when the electrolysis was carried out in baths consisting of a solution of K_2ZrF_6 in NaCl or KCl. Foreign workers recommend the use of a bath containing 20% K_2ZrF_6 + 80% NaCl /1/. Soviet workers pointed out the advantages of electrolytes containing 25 to 30% K_2ZrF_6 and 70 to 75% KCl (the decomposition potential of KCl is higher than that of NaCl; the solubility of KF in water is higher than the solubility of NaF, which facilitates the separation of the electrolyte from zirconium powder) /22/. The cathodic reaction involved in the electrolysis is:

$$ZrF_6^{2-} \rightleftarrows Zr^{4+} + 6F^-;$$
$$Zr^{4+} + 4e \rightarrow Zr.$$

Fluoride ions are discharged at the anode. However, the elemental fluorine reacts immediately with the chloride ions. Thus, chlorine is evolved at the anode. The anodic reaction is:

$$4F^- + 4NaCl - 4e \rightarrow 4NaF + 2Cl_2\uparrow.$$

Thus, potassium and sodium fluorides gradually accumulate in the bath. The optimum conditions of electrolysis in NaCl and KCl baths are similar.

A high degree of separation of zirconium from hafnium is obtained by electrolysis of fluoride-chloride melts. The potential of hafnium is lower than that of zirconium and hafnium accumulates in the melt. Thus, the cathodic deposit from a melt containing K_2ZrF_6 with 0.6% Hf (in % of the Zr + Hf) contains only 0.05% Hf /23/.

In order to produce high-quality zirconium powder, the fluozirconate used must be of a high degree of purity and the process must be carried out in a purified argon atmosphere.

The design of one type of hermetically sealed electrolyzer for the production of zirconium is shown in Figure 128. The pure graphite crucible, which is heated by means of a graphite heater, serves as the

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anode. A steel or molybdenum rod may be used as the cathode. A carbon-black packing is used as thermal insulation.

It is very important to dry in advance the crucible, the whole electrolyzer and the initial salts used in the process. The electrolyte is purified by preliminary electrolysis at a reduced potential (1.5 to 2V) using graphite cathode. This causes the deposition of metallic contaminants more noble than zirconium. The cathode is then replaced and the electrolysis is carried out at 750 to 860° at a potential of 3.5 to 4V and a current density of 2.5 to 4 amp/cm^2. The metal is deposited on the cathode in the form of coarse crystals 0.3 to 0.5 mm in size. The rate of deposition is 0.5 g/amp·hr, the current efficiency is 60 to 65%.

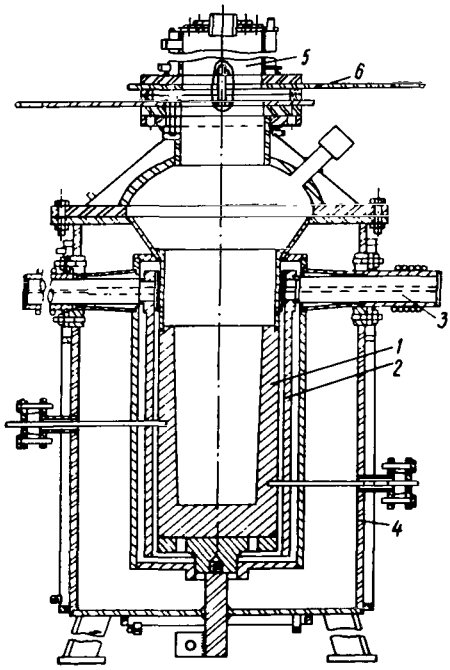

FIGURE 128. Diagram of a hermetically sealed electrolyzer for the production of zirconium.

1—graphite crucible serving as the anode; 2—graphite electrical heater; 3—heater electrodes; 4—hermetically sealed jacket; 5—chamber for cooling the cathodic deposit in argon; 6—shield.

When a sufficient amount of zirconium has collected, the cathode is lifted into the cooling chamber. The cathodic material contains about 25% zirconium and 75% salts (NaCl, KCl, KF, NaF). It is crushed and leached with hot water. The zirconium powder is rinsed with alcohol or acetone and dried. It has the following composition: 99.8 to 99.9% Zr, 0.03 to 0.05% C, 0.01 to 0.02% N, and 0.04 to 0.07% C.

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When graphite crucibles are used for the electrolysis, the duration of the electrolysis is limited by the gradual saturation of the graphite crucible with the melt. This drawback is eliminated in an electrolyzer developed by Soviet scientists. The bath is made of stainless steel and is cooled with water. The electrolyte in contact with the walls solidifies, creating a crust which protects the walls against corrosion /22/.

After remelting in vacuum the electrolytic zirconium has mechanical properties similar to those of zirconium produced by thermal reduction of zirconium chloride with magnesium.

If proper equipment for continuous or semicontinuous electrolysis is developed, the electrolytic production of zirconium will be able to compete with the method based on thermal reduction with magnesium.

69. THE THERMAL DISSOCIATION (IODIDE) METHOD /1, 6, 13, 14/

Zirconium of the highest degree of purity is usually produced by refining the metal by thermal dissociation of zirconium iodide; the nature of the process was described above in the chapter on titanium (see Section 51).

The iodide purification method is based on a reversible reaction which is carried out in a single vessel.

$$\underset{\text{crude}}{Zr} + 2I_2 \xrightarrow[\text{or } 470-550^\circ]{250-300^\circ} \underset{\text{(vapor)}}{ZrI_4} \xrightarrow{1300-1400^\circ} \underset{\text{purified}}{Zr} + 2I_2. \quad \text{(vapor)}$$

The rate of deposition of zirconium on the filament is determined by the rates of transfer of iodide to the filament surface and of iodine to the zirconium to be purified. This is the cause of the relatively low rate of the iodide process. Moreover, the process rate depends on the temperatures of the filament and of the crude zirconium. The optimum filament temperature is 1300°.

The zirconium being purified is maintained at 250 to 300 or 470 to 550°. A sharp drop in the process rate is observed at 300 to 450°. This is attributed to the interaction at these temperatures of ZrI_4 with zirconium, with the formation of the nonvolatile ZrI_3:

$$3ZrI_4 + Zr \rightarrow 4ZrI_3$$

with the result that the concentration of ZrI_4 in the gaseous phase decreases.

The vapor pressure of ZrI_4 increases above 450° because of the disproportionation of the lower chlorides:

$$2ZrI_3 \rightleftharpoons ZrI_2 + ZrI_4,$$

$$2ZrI_2 \rightleftharpoons ZrI_4.$$

Industrial equipment for the iodide process is made of a nickel-chromium alloy. Its design is the same as that described earlier (see Figure 106).

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In order to maintain the required temperature of the walls adjacent to the crude zirconium, the apparatus is immersed in a molten-salt thermostat. The filament temperature is controlled by the method described in the chapter on titanium.

Zirconium sponge (prepared by thermal reduction of the chloride with magnesium) or powder (prepared by reducing zirconium dioxide with calcium or by electrolysis) may be used as the starting material. About 50 g of iodine are introduced into the vessel for each kg of crude zirconium taken. A number of V-shaped zirconium filaments is usually mounted inside the vessel; the filament diameter is about 2 mm. Zirconium rods, 25 to 30 mm in diameter and up to 2 m long, are obtained at the end of the process. Up to 50 kg of purified zirconium is produced in one vessel. Depending on the conditions, a rod 25 mm in diameter can be grown within 30 to 40 hours.

The iodide purification process removes oxygen and nitrogen (since zirconium nitrides and oxides do not react with iodine) and metallic contaminants which do not form volatile iodides.

The concentration of impurities in zirconium produced by the iodide process is, %:

Si . . . $3 \cdot 10^{-3}$	Mn . . . $< 1 \cdot 10^{-3}$	Sn . . . $< 1 \cdot 10^{-3}$
Fe . . . $2 \cdot 10^{-2}$	Mg . . . $< 1 \cdot 10^{-3}$	N . . . $1 \cdot 10^{-3}$
Al . . . $3 \cdot 10^{-3}$	Pb . . . $< 1 \cdot 10^{-3}$	O . . . $1 \cdot 10^{-2}$
Cu . . . $< 5 \cdot 10^{-5}$	Mo . . . $< 1 \cdot 10^{-3}$	H . . . $1 \cdot 10^{-3}$
Ti . . . $1 \cdot 10^{-3}$	Ni . . . $1 \cdot 10^{-3}$	C . . . $1 \cdot 10^{-2}$
Ca . . . $< 5 \cdot 10^{-3}$	Cr . . . $3 \cdot 10^{-3}$	

70. PRODUCTION OF SOLID ZIRCONIUM

As in the case of titanium, solid zirconium is produced by melting in arc furnaces with consumable electrodes. The design of such furnaces has been described above (see Chapters II and IV). The electrodes are prepared in advance by pressing zirconium sponge. If necessary, the alloying additives are introduced during the melting. The melting is carried out in vacuo or in an inert gas atmosphere (argon, helium). In most cases uniform ingots are produced by remelting in which the ingot made in the first melting is used as the consumable electrode.

The melting rate is 110 kg/hr (for ingots 152 mm in diameter) and the consumption of electrical energy is 1.2 kwh/kg; in the case of ingots 254 mm in diameter the melting rate is 270 kg/hr and the consumption of electrical energy is about 0.8 kwh/kg.

A small fraction of the zirconium produced is compacted (mainly to yield small articles of irregular shape) by powder metallurgy methods. Zirconium hydride powders are preferentially used in powder metallurgy. Electrolytic powders and powders prepared from zirconium sponge (see chapter on titanium) may also be used.

The metal or hydride powders are pelletized by pressing under 6 to 8 tons/cm^2. The pellets are sintered in vacuo (10^{-4} to 10^{-5} mm Hg) at 1200 to 1300°.

Pellets with a density close to the theoretical, which may be pressure worked, are produced by using suitable sintering times. Zirconium alloys

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may also be produced by powder metallurgy. The metal produced by powder metallurgy usually has higher oxygen and nitrogen contents than the metal produced by vacuum melting of the sponge. It has a lower corrosion resistance.

The mechanical properties of solid zirconium prepared by various methods are compared in Table 42.

TABLE 42

Mechanical properties of zirconium prepared by the iodide process and by thermal reduction with magnesium

Zirconium type	Tensile strength kg/mm^2	Elongation of a 50.8 mm sample, %	Vickers hardness, kg/mm^2
Sponge made by thermal reduction with magnesium. Molten in arc furnace. Forged and rolled at 1000°, cold-rolled with 30% reduction. Annealed for 1 hour at 700°.	44.5	30	180
Prepared by the iodide process. Molten in arc furnace. Forged and rolled at 790°. Subsequent processing as for sponge zirconium.	25.0	36	104

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Part Two

THE RARE-EARTH METALS

Chapter VI

THE RARE-EARTH METALS (LANTHANIDES)

71. GENERAL DATA ON RARE-EARTH METALS

The place of the lanthanides in the periodic system and their electron structure /3, 10/

The lanthanide group comprises 14 elements with atomic numbers from 58 (cerium) to 71 (lutecium) which are located in row 6 of the periodic table following lanthanum, and whose properties resemble those of lanthanum. For this reason lanthanum is usually included in the group and the elements are known as lanthanides — e.g., resembling lanthanum. Moreover, scandium and yttrium, which belong to Group III, are chemical analogs of lanthanum, and which (especially yttrium) are almost always present together with lanthanides in minerals are also considered as lanthanides. Lanthanides usually have a place apart in the periodic table, at the bottom of the table (see Table 1). They all have very similar physicochemical properties. This is due to the peculiar structure of their electron shells. It is well known that the chemical and many physical properties of the elements depend mainly on the structure of the external electron shells. In the lanthanides the structure of the two outer shells (the *O* and *P* shells) remains the same as the charge on the nucleus (i.e., the atomic number) is increased, since the transition from one element to another is due to the filling of the inner 4*f*-electron level (see Table 43). The maximum number of electrons in the *f*-orbital is 14, and this is also the total number of the lanthanides.

The 4*f*-electrons are relatively unaffected by external factors since they are shielded by the electrons in the outer orbitals. Hence, they have little effect on the chemical properties of the lanthanides.

In the ground state the lanthanide atoms (except gadolinium and lutecium) have no electrons in the 5*d*-orbital (see Table 43). However, the transfer of an electron from the 4*f*- to the 5*d*-orbital requires a small amount of energy. The valency of 3+ characteristic of the lanthanides is associated with the transfer of one electrom the the 4*f*- to the 5*d*-orbital. The valency bonds then involve two electrons from the outer 6*s*-orbital and one electron from the 5*d*-orbital. In addition to the valency of 3+, some lanthanides may have valencies of 2+ or 4+ (Table 43). These "abnormal" valencies are attributed to the variation in the binding strengths of 4*f*-electrons with their number. The binding strength increases as the number of 4*f*-electrons varies from 1 to 7 and again from 8 to 14, i.e., the maximum binding strengths correspond to a half-filled and a completely

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filled 4*f*-orbital. Hence, gadolinium and lutecium have the most stable *f*-orbital configurations. A valency of 4+ is exhibited by cerium and praseodymium (the first *f*-electrons are easily transferred to the 5*d*-orbital) and terbium and dysprosium, which follow gadolinium in the series. A valency of 2+ is exhibited by samarium, europium, and ytterbium, i. e., in elements in which the number of electrons in the *f*-orbital is either equal or close to 7 or 14.

TABLE 43

Electron structure, valency, ionic radii and ionization potentials of the lanthanides

Atomic number and symbol	*N*-shell ($n=4$)				*O*-shell ($n=5$)			*P*-shell ($n=6$) 6*s*	Common valency	Ionic radius R^{3+} according to Goldschmidt, Å	Ionization potential $R^0 \rightarrow R^{3+}$, eV
	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*				
57La	2	6	10	—	2	6	1	2	3+	1.22	36.2
58Ce	2	6	10	2	2	6	—	2	3,4+	1.18	37.2
59Pr	2	6	10	3	2	6	—	2	3,4 (5?)+	1.16	37.5
60Nd	2	6	10	4	2	6	—	2	3+	1.15	37.8
61Pm	2	6	10	5	2	6	—	2	3+	—	38.2
62Sm	2	6	10	6	2	6	—	2	2,3+	1.13	38.2
63Eu	2	6	10	7	2	6	—	2	2,3+	1.13	38.8
64Gd	2	6	10	7	2	6	1	2	3+	1.11	38.6
65Tb	2	6	10	9	2	6	—	2	3,4+	1.09	39.4
66Dy	2	6	10	10	2	6	—	2	3(4)+	1.07	39.5
67Ho	2	6	10	11	2	6	—	2	3+	1.05	40.0
68Er	2	6	10	12	2	6	—	2	3+	1.04	40.2
69Tu	2	6	10	13	2	6	—	2	3(2)+	1.04	40.3
70Yb	2	6	10	14	2	6	—	2	2,3+	1.00	40.8
71Lu	2	6	10	14	2	6	1	2	3+	0.99	41.0

The lanthanides are subdivided into two groups: the cerium group [(La), Ce, Pr, Nd, Pm, Sm, and Eu] and the yttrium group [Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, and (Y)]. This subdivision was originally based on the differences in solubility between the double sulfates of the lanthanides and sodium or potassium. However, subsequent studies revealed periodic variations of some properties within the lanthanide series, which were in agreement with their separation into two subgroups.

Thus, there is an analogy in the variations of the valency states within the two subgroups (see Figure 129) and in the color of the ions: the color of solutions of the trivalent ions of the first seven elements resembles, in the reverse order, the color of the next seven elements (see Table 44). The variations in the magnetic properties of the trivalent ions also have a periodic nature (see Figure 130).

On the other hand, there are some properties that vary gradually within the series. Thus, the atomic and ionic radii decrease continuously as the atomic number is increased (see Table 43). This phenomenon, which is known as the "lanthanide contraction" is attributed to the gradual decrease in the basicity of the elements in the transition from cerium to

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lutecium and is the cause of the different solubilities of the lanthanides and the stability of their complex compounds.

TABLE 44

Color of the trivalent lanthanide ions

Atomic number	Number of electrons in the *f* orbital of the trivalent iron							
	$4f^0$ and $4f^{14}$	$4f^1$ and $4f^{13}$	$4f^2$ and $4f^{12}$	$4f^3$ and $4f^{11}$	$4f^4$ and $4f^{10}$	$4f^5$ and $4f^9$	$4f^6$ and $4f^8$	$4f^7$
57	La colorless							
58		Ce colorless						
59			Pr green-yellow					
60				Nd red-violet				
61					Pm pink			
62						Sm yellow		
63							Eu pale-pink	
64								Gd colorless
65							Tb pale-pink	
66						Dy pale-green-yellow		
67					Ho dark yellow			
68				Er pink				
69			Tu pale-green					
70		Yb colorless						
71	Lu colorless							

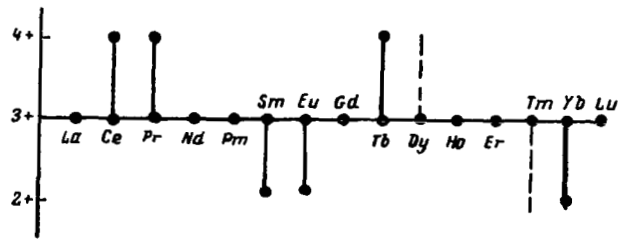

FIGURE 129. Valencies of the lathanide elements.

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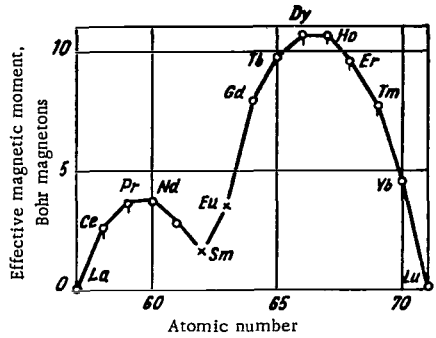

FIGURE 130. Magnetic moments of the trivalent lanthanide ions.

Brief historical note on the discovery of the lanthanides /1, 10/

The discovery of the lanthanides has a complicated history. The mixture of lanthanide oxides ("earths") isolated from minerals was originally believed to be a single element.

First discovered was the earth yttria, by the Finnish chemist Gadolin in 1794; it was found in the vicinity of Ytterby, Sweden, in a mineral which was subsequently named gadolinite. A few years later (in 1803) Klaproth and Berzelius simultaneously isolated a new "cerite earth" from the "heavy stone bastnäsite". For a long time yttria and ceria were believed to be the same earth and to belong to the same element. It was only in 1839 that Mosander isolated cerium oxide, lanthanum oxide, and "didymium" (a mixture of neodymium and praseodymium oxides) from ceria. Four years later he also isolated terbium and erbium oxides from yttria. The subsequent separation of the oxides and the discovery of new elements was accelerated by the discovery of spectroscopic analysis. In 1878 Marignac isolated ytterbium from erbia, and in 1879 Cleve found erbium, thulium and holmium in erbia. In the same year Lecoq de Boisbaudran prepared samarium from ceria, and in 1880 Marignac isolated gadolinium.

In 1873 Mendeleev was the first to use the fractional crystallization of the double ammonium nitrates for the separation of lanthanum and "didymium". Using the same method, von Welsbach showed in 1885 that "didymium" is a mixture of neodymium and praseodymium. Dysprosium, europium, and lutecium were discovered later. Only the element with the atomic number $Z=61$ remained undiscovered in 1907. As we know now, this can be attributed to the fact that it has no stable isotopes. Element 61 was prepared only in 1947 (by Marinsky and Glendenin) from the uranium fission products in a reactor, and was named by them promethium. The isolated promethium isotope with a mass number of 147 has a half-life of about 3.7 years.

Although the discovery of the lanthanides was completed towards the beginning of the twentieth century, many of them were not isolated in pure form and they were not thoroughly studied. New, more effective methods for the separation of the lanthanides have been developed within the last 15 years.

By now all the lathanides have been prepared both as pure compounds and pure metals.

Physical properties /7, 10, 12/

The lanthanides are silvery-white metals. Some of them are pale-yellow (e. g., praseodymium and neodymium). They have close-packed hexagonal or face-centered cubic crystal lattices, with the exception of samarium (rhombohedral) and europium (body-centered) (Table 45). La, Ce, Pr, Nd, Sm, Gd, Tb, and Yb have more than one allotropic modification.

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TABLE 45

Physical properties of the lanthanides, yttrium and scandium*

Element	Atomic number	Density (X-ray) g/cm³	Melting point, °C	Approximate boiling point, °C	ΔH of vaporization (at 25°C) kcal/mole	C_p at 0°C cal/mole·deg	Specific resistance (at 25°C) ohm·cm·10⁻⁶	Thermal neutron capture cross section barns	Crystalline structure	Lattice parameter, Å	Average atomic radius (for coordination No.12), Å	Electron work function, eV	Electrode potential $R^0 - R^{3+}$, V	Modulus of elasticity, kg/mm²	Tensile strength, kg/mm²
α-La	57	6.162	920 ± 5	3470	99.5	6.27	56.8	8.9	Close-packed hexagonal	a = 3.770 c = 12.159	1.877	3.33	-2.4	3915	11.2
γ-Ce	58	6.768	804 ± 5	3470	97.6	6.37	75.3	0.70	Face-centered cubic (Cu type)	a = 5.1612	1.825	2.84	-2.335	3058	10.3
α-Pr	59	6.769	935 ± 5	3017	84.7	6.38	68.0	11.2	Close-packed hexagonal (Mg type)	a = 3.6725 c = 11.8354	1.828	2.7	-2.2	3592	8.9
α-Nd	60	7.007	1024 ± 5	3210	75.6	6.52	64.3	44	The same	a = 3.6579 c = 11.7992	1.821	3.3	-2.246	3860	13.9
α-Sm	62	7.536	1072 ± 5	1670	50.6	11.80	88	6500	Rhombohedral	a = 8.996 α 23°13'	1.802	3.2	-2.2	3480	—
Eu	63	5.245	826 ± 10	1430	42.2	6.20	81.3	4500	Body-centered cubic (W type)	a = 4.5820	2.042	2.54	-2.2	—	—
α-Gd	64	7.886	1312 ± 15	2830	80.9	9.633	140.5	44,000	Close-packed hexagonal (Mg type)	a = 3.6360 c = 5.7826	1.802	3.07	-2.2	5730	15.9
α-Tb	65	8.253	1368 ± 10	2480	72.0	7.136	—	44	The same	a = 3.6010 c = 5.6936	1.782	3.09	-2.2	5864	—
Dy	66	8.559	1380 ± 20	2330	69.8	6.72	56	1100	"	a = 3.5903 c = 5.6475	1.773	3.09	-2.2	6433	24.4
Ho	67	8.779	1500 ± 25	2380	69.0	6.45	87	64	"	a = 3.5773 c = 5.6158	1.776	3.09	-2.1	6850	—
Er	68	9.062	1525 ± 25	2390	73.6	6.66	107	166	"	a = 3.5588 c = 5.5874	1.757	3.12	-2.1	7474	19.5

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Tu	69	9.318	1600 ± 50	1720	58.4	6.50	79	118	"	a = 3.5375	1.746	3.12	-2.1	—	—			
										c = 5.5546								
α-Yb	70	6.953	824 ± 5	1320	41.5	6.32	27	36	Face-centered cubic (Cu type)	a = 5.4862	1.940	2.59	-2.1	1815	—			
Lu	71	9.849	1675 ± 25	2680	77.0	6.23	79	108	Close-packed hexagonal (Mg type)	a = 3.5031	1.734	3.14	-2.1	—	—			
α-Sc	21	2.985	1538 ± 20	2900	80.8	6.00	—	13	The same	c = 5.5509 a = 3.3090	1.641	3.23	—	—	—			
										c = 5.2733								
Y	39	4.472	1525 ± 25	3025	80.0	6.13	69 ± 3	1.38	"	a = 3.6474 c = 5.7306	1.801	3.07	—	6700	14.0			

* Except where otherwise noted the structure, density and other properties given are for the modification which is stable at room temperature.

Some of the physical properties of the lanthanides are shown in Table 45. The melting points of the elements belonging to the cerium subgroup are much lower than those of the elements of the yttrium subgroup. It is noteworthy that the boiling points of Sm, Eu, and Yb, which may have a valency of 2+, are much lower than those of the other lanthanides. Mention must be made of the large thermal neutron capture cross sections of gadolinium, samarium, and europium.

The pure lanthanides are ductile and are worked without difficulty (by forging, rolling). The mechanical properties are strongly affected by the concentration of impurities, and especially of oxygen, sulfur, nitrogen, and carbon. The tensile strengths and moduli of elasticity of the metals in the yttrium subgroup (except ytterbium) are higher than those of the metals of the cerium subgroup (Table 45).

All the lanthanides are paramagnetic, except Gd, Dy, and Ho, which have ferromagnetic properties. α-Lanthanum becomes superconducting at 4.9°K and β-La at 5.85°K. The remaining lanthanides do not become superconducting even if the temperature is reduced to a fraction of 1°K.

Chemical properties /1, 2/

The lanthanides are characterized by their high chemical activity. They form very stable oxides, halides, and sulfides, and react with hydrogen, carbon, carbon-containing gases, nitrogen, phosphorus, and a number of other elements.

The metals are decomposed by water (slowly in the cold, and more rapidly in hot water) and readily dissolve in hydrochloric, sulfuric, and nitric acids. The lanthanides are not attacked by hydrofluoric and phosphoric acids because of the formation of protective films of sparingly soluble salts.

Lanthanum, cerium, praseodymium, and neodymium are rapidly attacked by dry and humid air at room temperature, while other metals are attacked slowly and retain their metallic luster for a long time. Cerium differs from the other

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lanthanides in having an oxide Ce_2O_3 which is easily oxidized to the dioxide CeO_2; as a result cerium and cerium-rich alloys are pyrophoric. All lanthanides are rapidly oxidized in air at temperatures above 180 to 200° with the formation of oxides of the type Ln_2O_3 (except cerium, praseodymium, and terbium which form CeO_2, Pr_6O_{11}, and Tb_4O_7).

TABLE 46

The melting and boiling points of lanthanide fluorides and chlorides of the LnX_3 type, in °C /2/

Element	Fluorides		Chlorides	
	melting	boiling	melting	boiling
La	1430	2330	855	1750
Ce	1465	2330	805	1730
Pm	1373	2330	779	1710
Nd	1413	2330	778	1690
Pr	1410	2330	740	1670
Sm	1400	2330	681	Decomposes
Eu	1390	2280	626	»
Gd	1380	2280	612	1580
Tb	1370	2280	591	1550
Dy	1360	2230	657	1530
Ho	1360	2230	721	1510
Er	1350	2230	777	1500
Tu	1340	2230	824	1490
Yb	1330	2230	857	Decomposes
Lu	1320	2230	895	1480
Y	1390	2230	703	1510

The lanthanide oxides are characterized by their chemical stability and high melting points. For instance, CeO_2 melts at about 2500° and La_2O_3 above 2000°.

Ce_2O_3, Pr_2O_3, and Nd_2O_3 have hexagonal crystal lattices, while the oxides of the other lanthanides have cubic lattices.

The Ln_2O_3 oxides of La, Ce, Gd, Tb, Dy, Lu, and Y are colorless; Tu_2O_3 is white with a greenish hue; Ho_2O_3 is pale-yellow, Pr_2O_3 is greenish-yellow, Eu_2O_3 is pale-pink, Er_2O_3 is pink, Nd_2O_3 is lilac-colored, Tb_4O_{11} is dark-brown, Pr_6O_{11} is black-brown, and CeO_2 (when free from other lanthanides) is yellow when hot and white when cold.

Lanthanides absorb hydrogen even at room temperature and react rapidly with hydrogen at 250 to 300° with the formation of hydrides of the type $LnH_{2.8}$ (for Ce, La, and Pr) or LnH_2. The hydrides decompose when heated in vacuo (to above 1000°) and are unstable in humid air. Nitrogen reacts with lanthanides at 750 to 1000°, yielding nitrides, mostly of the RN type. Their properties have not been thoroughly studied. The lanthanides react with hot carbon, hydrocarbons, Co and CO_2 yielding carbides of the LnC_2 type. The carbides are unstable in air and decompose water, yielding hydrocarbons (mostly acetylene, and some methane). The sulfides (Ln_2S_3, Ln_3S_4 and LnS) are formed when the lanthanide metals are heated in sulfur vapor. The sulfides have high melting points and are fire-resistant. The melting points of some sulfides are: La_2S — 2100°, Ce_3S_4 — 2500°, and Nd_2S_3 — 2200°.

At temperatures above 200° all halogens react rapidly with lanthanides. The halides formed (of the LnX_3 type) have relatively high melting and boiling points (Table 46).

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The halides (except the fluorides) are hygroscopic and readily hydrolyze with the formation of oxyhalides LnOX. Lower halides (LnX_2) are known to exist only in the cases of samarium, europium, and ytterbium.

The properties of lanthanide compounds isolated from solutions

The lanthanide hydroxides $Ln(OH)_3$ are basic and are sparingly soluble in water and alkalies. Because of the decreasing basicity in the transition from cerium to lutecium, there is a decrease in the pH at which the hydroxides start to precipitate and in their solubility products (Table 47).

TABLE 47

The pH of precipitation and the solubility product of hydroxides of the $Ln(OH)_3$ type

Element	pH of precipitation of nitrate solution	Solubility product of $Ln(OH)_3$ at 25°	Element	pH of precipitation of nitrate solution	Solubility product of $Ln(OH)_3$ at 25°
La	7.82	$1.0 \cdot 10^{-19}$	Gd	6.83	$2.1 \cdot 10^{-22}$
Ce	7.60	$1.5 \cdot 10^{-20}$	Er	6.75	$1.3 \cdot 10^{-23}$
Pr	7.35	$2.7 \cdot 10^{-20}$	Tu	6.40	$3.3 \cdot 10^{-24}$
Nd	7.31	$1.9 \cdot 10^{-21}$	Yb	6.30	$2.9 \cdot 10^{-24}$
Sm	6.92	$6.8 \cdot 10^{-22}$	Lu	6.30	$2.5 \cdot 10^{-24}$
Eu	6.82	$3.4 \cdot 10^{-22}$	Y	6.95	—

The hydroxide of Ce^{4+} is precipitated from solution at pH 0.9 to 1, and cerium may be separated from the other lanthanides in this way (after oxidation of Ce^{3+} to Ce^{4+}).

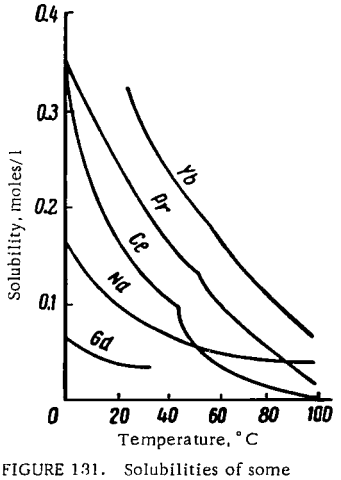

FIGURE 131. Solubilities of some lanthanide sulfates at various temperatures.

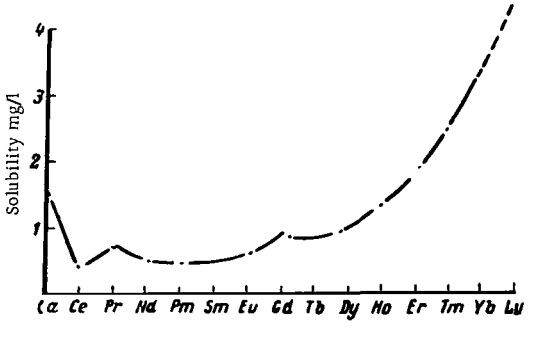

FIGURE 132. Solubility of lanthanide oxalates in water at 25°C.

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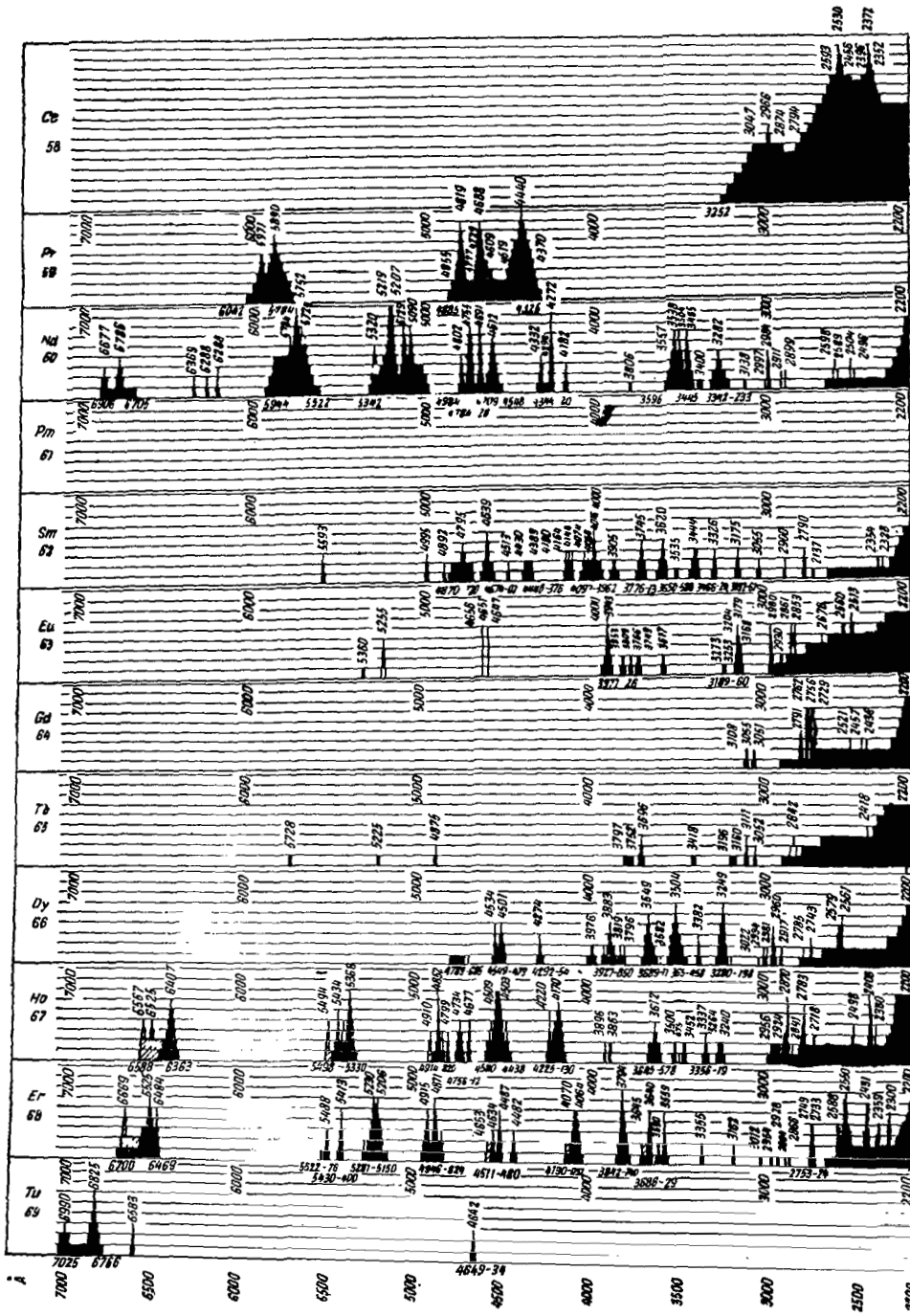

FIGURE 133. Absorption spectra of solutions of chlorides of trivalent lanthanides.

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The chlorides, sulfates, and nitrates of the trivalent lanthanides are soluble in water and in most cases crystallize as crystalline hydrates of variable composition. The solubility of the sulfates $Ln_2(SO_4)_3 \cdot 8H_2O$ decreases sharply as the temperature is increased from 0 to 100° (Figure 131).

The fluorides and oxalates are sparingly soluble in water and dilute inorganic acids. The fluorides are precipitated either as the crystalline hydrates $LnF_3 \cdot 0.5H_2O$ (La, Ce, etc.) or anhydrous salts (e. g., of Pr and Nd). The most common composition of the oxalates is $Ln_2(C_2O_4)_3 \cdot 10H_2O$. The oxalates of the lanthanides of the yttrium subgroup are more soluble in water than are the oxalates of the cerium subgroup (Figure 132). When heated to 500 to 600° the oxalates decompose yielding oxides of the Ln_2O_3 type.

The lanthanide phosphates, carbonates, and ferricyanides are also sparingly soluble in water.

Most of the simple lanthanide salts have a tendency towards the formation of double or complex salts with ammonium and alkali metal salts and with a number of salts of bivalent elements. The most important of these are: the double nitrates of the lanthanides with ammonium nitrate $Ln(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ and magnesium nitrate $2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, whose solubilities increase in the transition from lanthanum to gadolinium; the double lanthanide potassium (or sodium) sulfates (e. g., $Ln_2(SO_4)_3 \cdot MeSO_4 \cdot nH_2O$ where n is 1 or 2). From the standpoint of their solubility in water, double lanthanide sulfates can be subdivided into three groups: sparingly soluble (La, Ce, Pr, Nd, Sm), of medium solubility (Eu, Gd, Tb, Dy) and readily soluble (Ho, Er, Tu, Yb, Lu, Y). This is extensively used for the advance separation of the lanthanides into the cerium and yttrium subgroups.

The lanthanides form complex compounds with many organic substances. The most important are the complexes with citric acid and with a number of aminopolyacetic acids: nitrilotriacetic acid (NTA), ethylene diamine tetraacetic acid (EDTA) and some other so-called "complexones" (see p. 356). In most cases the stability of the organic acid complexes of the lanthanides increases from La to Lu, which is the principle of some methods of separation of the lanthanides. The lanthanide compounds are characterized by the fact that their absorption spectra are composed of sharp bands and lines. The relative intensities of the bands in the wavelength range from 2000 to 7000 Å are shown in Figure 133. In the visible (3900 to 7700 Å), the Ce^{3+}, Gd^{3+}, La^{3+}, Lu^{3+}, and Yb^{3+} ions are colorless. The remaining lanthanide ions display characteristic colors.

Uses of rare-earth metals /4/

The lanthanides are used as metals, alloys, and chemical compounds in various branches of technology: ferrous and nonferrous metallurgy, production of glass and ceramics, the chemical industry, medicine, and agriculture. They still have other potential uses, the number of which increases as the properties of lanthanides, their alloys, and compounds become known.

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Ferrous and nonferrous metallurgy. The lanthanides find extensive use as additives in the production of steel, pig iron, and nonferrous metal alloys. They are used mainly as ferrocerium or mischmetall (a lanthanide alloy in which the main components are cerium or cerium and lanthanum). *Lanthanide oxides are also used as additivies*/5/.

The addition of lanthanides improves the quality of stainless and high-speed steels, high-silicon steels used in electrical technology, and refractory steels; they increase the mechanical strength (and especially the impact strength), corrosion resistance, and refractoriness, improve the workability of the steels, the surface of castings, and increase the recrystallization (grain growth) temperature of steel. From 0.9 to 2.25 kg of mischmetall is usually added per ton of steel. The addition of cerium or mischmetall causes deoxidation, desulfurization, and probably denitridization of the steel.

The lanthanide metals also improve the quality of pig iron (casting properties, hot ductility, resistance to oxidation, and strength).

The addition of 0.35% mischmetall to nichrome prolongs its service life at 1000° by a factor of 10.

Ferrous alloys with a high concentration of cerium group metals (70 to 75% lanthanides and 25 to 30% Fe) are pyrophoric and find extensive use in the production of flints (for lighters) and are used in artillery for tracer compositions. Mischmetalls or a mischmetall alloy with tin and magnesium may also be used for similar purposes.

The addition of lanthanide metals to various aluminum and magnesium alloys increases their high-temperature strength. Aluminum-copper and aluminum-copper-silicon alloys containing 0.05 to 0.35% cerium are used for the production of various aircraft engine parts. The introduction of mischmetall increases the creep strength of the high-strength fine-grained magnesium alloys (with zinc and zirconium) used in aviation. These magnesium alloys contain 0.5 to 4% Zn, 0.6 to 0.7% Zr, and 1.25 to 2.75% lanthanides.

The production of glass and ceramics. The glass industry is one of the major consumers of lanthanides.

The introduction of lanthanides in the composition of glass produces glasses which absorb ultraviolet and infrared light. Glass containing 2 to 4% Ce_2O_3 is used for the production of protective goggles for glass-blowing and welding works. Praseodymium and neodymium have a similar effect.

Cerium-containing glass is resistant (does not fog) under the effect of radioactive radiation. It is used in nuclear technology.

Some lanthanide oxides are used in the production of optical glass. Thus, La_2O_3 is one of the components of silicon-free glass for photographic lenses and periscopes. Nd_2O_3 together with V_2O_5 are added to optical glass for photometers, Nicol prisms and other instruments.

Lanthanide oxides have been used for a long time as decolorizers and colorants of glass. Thus, the addition of a small amount of CeO_2 decolorizes glass while the addition of up to 1% of cerium oxide makes the glass yellow while the addition of larger amounts makes it brown. Neodymium oxide colors the glass bright red, praseodymium oxide green, and a mixture of both produces a blue color.

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Lanthanide oxides are extensively used in the optical industry as abrasives in the polishing of glass. Cerium dioxide is used preferentially for this purpose (it is known as "Polirit") in the form of powders of various particle sizes which are obtained by varying ignition temperature. As polishing material CeO_2 is superior to the conventional polishing material ("rouge") from the standpoints of polishing speed and quality.

In ceramic industry lanthanide oxides are used as colorants and opacifiers for porcelain, glazes, and enamels. The use of lanthanide sulfides and oxysulfides as refractory and inert substances for the production of metal-melting crucibles is contemplated.

Nuclear technology. Lanthanides with a large thermal neutron capture cross section — gadolinium, samarium, and europium (see Table 45) — are of utmost importance for nuclear technology. The oxides of these metals are components of ceramic shields used in atomic reactors and nuclear engines.

Lanthanum salts are used as coprecipitants ("carriers") for the precipitation and separation of the transuranium elements formed in atomic reactors (e. g., for the separation of plutonium from uranium, and isolation of neptunium).

Electronics, X-ray and radio technology. In electronics lanthanides are used as components of nonsputtering gas absorbers (getters). Thus, one of the widely-used gas absorbers of the TsETO type consists of a finely-divided and sintered mixture of mischmetall with aluminum and thorium (80% Th, 14.5% mischmetall and 5.5% Al). Thorium actively absorbs hydrogen, but as an absorber of nitrogen it is less active than cerium and lanthanum.

Neodymium oxide is used in electronic devices as a dielectric with a low linear expansion coefficient.

Thulium has recently found a very important use; upon irradiation with reactor neutrons it becomes a source of γ-radiation. The radioactive isotope (Tm^{170}) formed as a result of the irradiation is used for the production of portable sources of soft X-rays for medical use and defectoscopy to replace the bulky X-ray equipment. Such instruments consume only 0.1 to 0.2 g of thulium oxide over a service life of one year (the half-life of Tm^{170} is 129 days). The activity of thulium preparations may be regenerated by repeating the irradiation.

The promethium isotope Pm^{147} (half-life 2.7 years) is used for the production of nuclear "microcells" in which the soft β-radiation of the promethium is converted into electrical energy. Such microcells may be used in miniature receivers, hearing aids, and devices for rockets, artificial satellites, etc.

Electric illumination technology. In this industry lanthanide fluorides have been in use for a long time for the production of carbon electrodes for searchlights and movie projectors; the lanthanides increase the illumination intensity. The fluorides (mainly CeF_3) are introduced as components of the central part of the electrode (the "core").

Chemical and light industry. Lanthanide compounds are used in the production of lacquers, paints, and phosphorescent compositions (phosphors) as catalysts for the synthesis of ammonia and oxidation processes in organic chemistry and as chemical reagents in analytical chemistry and photochemistry.

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Various lanthanide compounds are used for coloring and tanning of leather, and in the textile industry as mordants and water-proofing agents.

Agriculture. Lanthanide compounds have been recently used in agriculture as insectofungicides (pest control agents) and as microfertilizers to accelerate plant growth.

72. OCCURRENCE /14/

The natural resources of lanthanides are quite large. Their total content in the Earth's crust is 0.01%, i. e., the same as the content of copper. The most common lanthanides are La, Ce, and Nd. Lanthanides with odd atomic numbers are less abundant than their immediate neighbors with even atomic numbers (see Figure 134).

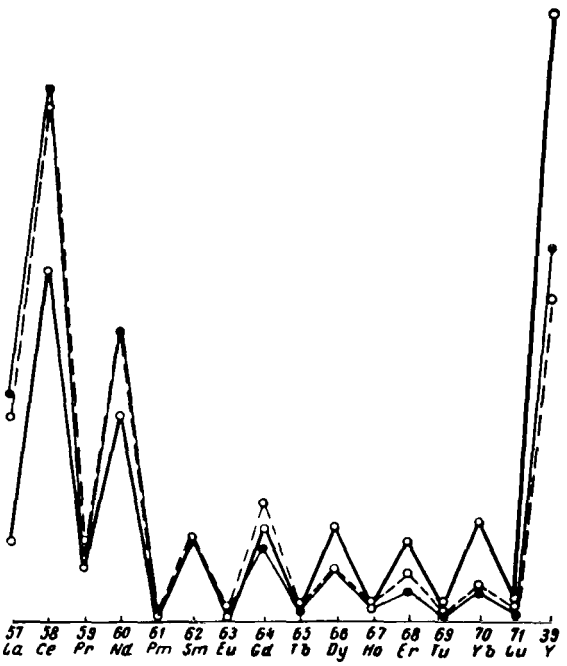

FIGURE 134. Abundance of lanthanides in the Earth's crust, according to Fersman (thick line), Gol'dshmidt (thin line), and Vinogradov (dotted line).

More than 250 lanthanide-containing minerals are known. Of these, 60 to 65 are lanthanide minerals, i. e., minerals in which the total concentration of the lanthanide elements is higher than 5 to 8%. These minerals consist of phosphates, fluorides or fluocarbonates, silicates and silicotitanates, niobotantalates and titanoniobates. The minerals usually contain some thorium and occasionally some uranium (Table 48).

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TABLE 48

The composition of some lanthanide minerals

Mineral	Formula	Approximate composition	Density, g/cm^3
Monazite	$(Ce, La...)PO_4$	50—60% $(Ce, La...)_2O_3$, 22—31.5% P_2O_5, 4—12% ThO_2, 0.1—0.5% U, occasionally ZrO_2 (up to 7%) and SiO_2 (up to 6%)	4.9—5.5
Xenotime	YPO_4	52—62.6% Y_2O_3 contaminated with Ce, Er, and other lanthanides, occasionally ThO_2, UO_2 (up to 5%), ZrO_2 (up to 3%), SnO_2, SiO_2 (up to 9%)	4.45—4.59
Bastnäsite	$(Ce, La...)FCO_3$	73—77%$(Ce, La, Pr)_2O_3$, 6.2—8.5% F, 19.8— 20.2% CO_2	4.8—5.2
Gadolinite	$Y_2FeBe_2Si_2O_{10}$	10—13.7% FeO, 30.7—46.5% Y_2O_3, 5—23%$(Ce, La...)_2O_3$, 23—24.5% SiO_2, 0.3—0.4% ThO_2, 9—10.2% BeO, impurities: Ca, Mg	4.1—4.5
Orthite (allanite)	$(Ca, Ce...)_2 \cdot (Al, Fe)_3 \times Si_3O_{12}(O, OH)$	Up to 6%Ce_2O_3, up to 7% $(La, Ce)_2O_3$, occasionally BeO (up to 3.8%), up to 8% Y_2O_3 (yttroorthite), impurity: ThO_2	4.1
Loparite	$(Na, Ca, Ce...)_2 \times (Ti, Nb, Ta)_2O_6$	39.2—40%TiO_2, 32—34% $(Ce, La...)_2O_3$, 8—10% $(Nb, Ta)_2O_5$, 4.2—5.2% CaO, 7.8—9%Na_2O, impurities: Sr, K, Si, Th (0.5—0.6%)	4.5—4.89
Euxenite-polycrase*	$(Y, Ce, Ca...) \times (Ti, Nb, Ta)_2O_6$	18.2—27.7%$(Y, Er...)_2O_3$, 0.2—4.3% $(Ce, La...)_2O_3$, 16—30%TiO_2, 4.3—41.4% Nb_2O_5, 1.3— 23% Ta_2O_5, 1—5% ThO_2, 0.4—12% UO_2	4.78—5.37
Fergusonite	$(Y, Er, Ce, U) \times (Nb, Ta, Ti)O_4$	46—57.5%$(Nb, Ta)_2O_5$, 31.42% Y_2O_3, 0.9—6%$(Ce, La...)_2O_3$, up to 14%Er_2O_3, 1—3.4% ThO_2, 1.2—6% UO_2, up to 6% TiO_2, impurities: ZrO_2, SnO_2, WO_3	5.58—6.23
Samarskite	$(Y, Er...)_4 \cdot (Nb, Ta)_6O_{21}$	6.4—14.5% Y_2O_3, 2.7—13.4% Er_2O_3, up to 8%$(Ce, La...)_2O_3$, 27.7—46.8% Nb_2O_5, 1.8—27.0% Ta_2O_5, 0.4—2% ThO_2, 4—16% UO_2, impurities: Ti, Zr, Sn, and others	5.6—5.8

* The mineral is known as polycrase when the $(Nb, Ta)_2O_5 : TiO_2$ ratio is 1 : (4—6) or lower, and as euxenite when the ratio is higher than 1 : 3.

There are wide fluctuations in the respective proportions of the individual lanthanides in minerals. Some minerals contain mostly the elements of the cerium group and only up to 5% of the yttrium earths (e. g., monazite, bastnäsite and loparite), while in others the elements of the yttrium group are predominant (e. g., xenotime, euxenite, and gadolinite).

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The lanthanides accumulate in various types of magmatogenic, sedimentary and metamorphogenic deposits*. Until the present the lanthanide industry has been based mainly on the exploitation of monazite placers and deposits containing the mineral b a s t n ä s i t e (bastnäsite-calcite veins).

One of the main sources of elements of the cerium subgroup is m o n a z i t e, which is usually found in pegmatites, and occasionally in granites and gneisses. As the bedrock is decomposed, the monazite passes into river and submarine placers together with ilmenite, zircon, magnetite, and other minerals.

The lowest monazite concentration in the worked placers is about 1%. The largest deposits have been found in India, Brazil, the USA, Australia, Madagascar, and Ceylon. Monazite concentrates containing 58 to 65% Ln_2O_3 are prepared by gravitational and magnetic beneficiation methods. From these, the lanthanides are isolated as by-products in the extraction of thorium.

The approximate composition of monazite concentrates is shown below (in %):

$\Sigma(Ln)_2O_3 + Y_2O_3$	58—65	Other $(Ln)_2O_3+Y_2O_3$	1—2
Ce_2O_3	21—30	ThO_2	3.5—6.5
La_2O_3	16—18	U_3O_8	0.15—0.3
Pr_2O_3	3—4	P_2O_5	26—30
Nd_2O_3	10—12	Fe_2O_3	0.5—0.8
Sm_2O_3	1—1.5	TiO_2	0.2—1.7
		SiO_2	1—2

L o p a r i t e is one of the minerals of commercial value; it has a complex composition and occurs in nepheline syenties and in many pegmatite veins. Loparite ores are easily enriched yielding concentrates which contain 80 to 90% of the mineral. In the processing of these ores the lanthanides are extracted together with niobium, tantalum, and titanium.

Fergusonite and xenotite are among the minerals used as a rich raw material for the extraction of lanthanides of the yttrium group.

73. PROCESSING OF MONAZITE CONCENTRATES

Monazite is the main raw material for the production of lanthanides and thorium. The processing of monazite yields two types of products: thorium concentrates and a technical grade mixture of lanthanide compounds.

Two methods for the decomposition of monazite concentrates are used in industrial practice:

1) decomposition with sulfuric acid;
2) decomposition with sodium hydroxide solutions.

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* Metamorphogenic deposits are deposits which have undergone changes (outside the weathering zone) after their formation; these changes cause, in particular, a partial or total recyrstallization of the rocks with the formation of new structures and minerals.

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The sulfuric acid method /10, 15/

This method of processing monazite is based on the decomposition of the concentrate by concentrated sulfuric acid followed by the leaching of lanthanide sulfates and thorium sulfate with water. The thorium and lanthanide compounds are then isolated separately from the solution.

Decomposition. The crushed monazite concentrate (particle size ~ 0.15 to 0.1 mm) is decomposed with concentrated sulfuric acid at 180 to 200°. The consumption of sulfuric acid depends on the composition of the concentrate and is of the order of 1.5 to 2 tons/ton of concentrate, which is 2.5 to 3 times more than the stoichiometric amount. It must be remembered that part of the sulfuric acid is lost through evaporation. Depending on the particle size of the concentrate the decomposition time ranges from 2 to 4 hours. The decomposition is carried out in batch reactors (made of steel or cast iron) fitted with a stirrer or in rotary-drum processers with automatic feeding of the sulfuric acid and the concentrate and with continuous discharge of the product. Measures must be taken for the quantitative absorption of sulfuric acid vapors by means of scrubbers or electrostatic filters.

In batch reactors, the concentrate is poured gradually, with stirring, into sulfuric acid preheated to 200°. At the end of the decomposition, the product is a paste-like mass with a dark-gray color. The material remaining after a more thorough separation of sulfuric acid (e. g., when the decomposition is carried out in continuous drum-type processers) is light gray or almost white. A higher degree of dehydration of silicic acid is obtained in such cases, and this facilitates the filtration of solutions in subsequent stages.

The main reactions involved in the decomposition are:

$$2\,(Ln)\,PO_4 + 3H_2SO_4 \rightarrow (Ln)_2\,(SO_4)_3 + 2H_3PO_4,$$
$$Th_3\,(PO_4)_4 + 6H_2SO_4 \rightarrow 3Th\,(SO_4)_2 + 4H_3PO_4.$$

The titanium minerals — ilmenite and rutile — are also decomposed by sulfuric acid, yielding titanium sulfates.

After the completion of the decomposition the resulting mass is leached in lead-lined steel reactors with cold water at a ratio of about 10 l of water per kg of concentrate to be decomposed. Such dilution is necessary in order to ensure the dissolution of the thorium and lanthanide sulfates. Towards the end of the leaching the temperature of the solution must not exceed 20 to 25° since the solubility of lanthanide sulfates decreases sharply with increasing temperature (see Figure 131).

The insoluble residue contains silica, zircon, cassiterite and some unreacted monazite. In addition, it usually contains a large fraction of the radioactive daughter products of thorium and uranium.

The solid residue is separated from the solution by settling and filtration and is then rinsed with cold water. The filtrate obtained contains the lanthanides, thorium, phosphoric acid, excess sulfuric acid, and contaminants such as titanium, iron, etc. The filtration of the solution is made difficult because of the presence of colloidal silicic acid. As a result, in some plants the pulp is filtered through a layer of sawdust.

The filtrate usually contains one of the thorium decomposition products — mesothorium (a radium isotope). It is isolated from the solution by the

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addition of barium chloride. The barium sulfate formed serves as a carrier for the coprecipitation of the isomorphous radium sulfate.

Isolation of thorium and lanthanides from the sulfate solutions. The various technological methods of processing monazite concentrates with sulfuric acid differ in the methods of isolation of the thorium concentrate and the lanthanide concentrate from the sulfate solutions.

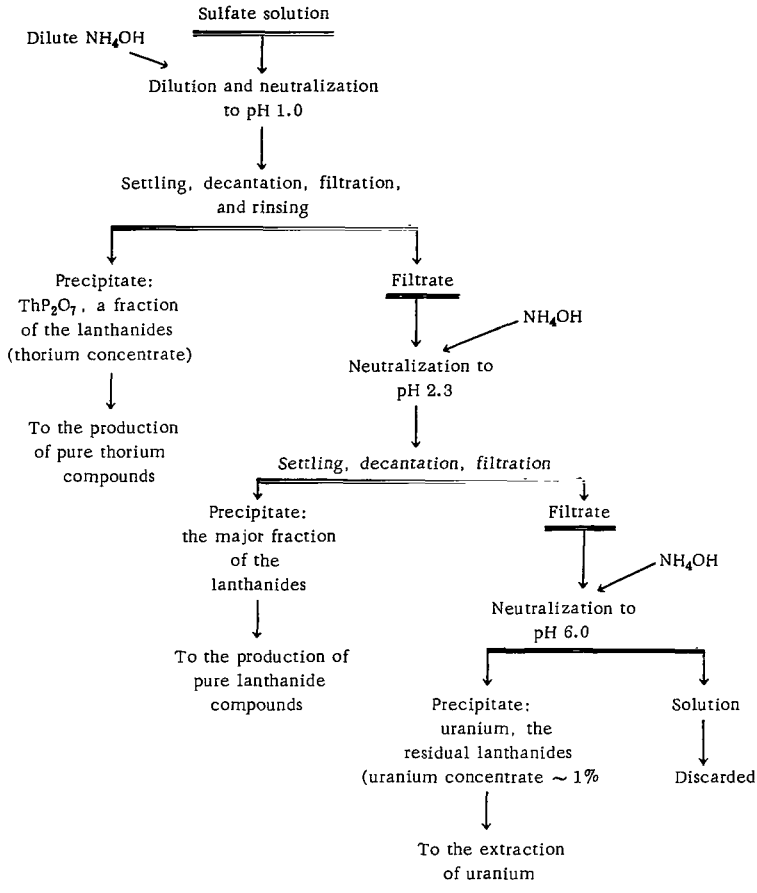

FIGURE 135. Flow sheet of the processing of sulfate solutions by the stepwise neutralization method.

The most widely used method is based on a stepwise neutralization of the solutions with the precipitation of thorium and lanthanide phosphates, taking advantage of the different pH of precipitation of thorium phosphate and lanthanide phosphates: thorium phosphate is precipitated from sulfate solutions at pH 1.0 while the lanthanide phosphates are precipitated at pH $\approx$ 2.3. A flow sheet of the process is shown in Figure 135.

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The neutralization is usually carried out with dilute solutions of ammonium hydroxide which are gradually added into the stirred sulfate solution. The thorium is separated by neutralizing the solution to pH 1 and heating to a boil. About 99% of the thorium is precipitated as the sparingly soluble thorium pyrophosphate $ThP_2O_7 \cdot 2H_2O$. Towards the end of the neutralization the total concentration of lanthanides in the solution must not exceed 2% in order to keep the sparingly soluble double lanthanide ammonium sulfates in solution. Nevertheless, 5 to 8% of the lanthanides (in % of the total amount present in the solution) is coprecipitated with the thorium.

Since the starting solution contains a much larger amount of lanthanides than of thorium, the precipitate usually contains about 50% of thorium phosphate and the rest is lanthanide sulfates (and possibly phosphates) which are sorbed by the voluminous precipitate. After the separation of the precipitate of thorium phosphate the solution is neutralized with ammonia to pH 2.3. This causes precipitation of the major fraction of the lanthanides, probably as acid phosphates of the $Ln_2(HPO_4)_3$ type. After settling, the precipitate is separated by filtration and used for the production of pure lanthanide compounds (see below). The filtrate which contains certain amounts of lanthanides and uranium is neutralized with ammonia to pH 6.0, which causes precipitation of uranyl hydroxide together with the lanthanides remaining in the solution. The precipitate contains up to 1% U and serves as the concentrate used for the extraction of uranium.

The composition of the precipitates and the distribution of thorium, lanthanides and uranium in the fractions from the stepwise neutralization of sulfate solutions is shown in Table 49 as an illustrative example.

TABLE 49

Composition of precipitates and distribution of thorium, lanthanides, and uranium in the fractions from the stepwise neutralization of sulfate solutions /16/

Product	pH of precipitation	Composition of precipitates, converted into oxide mixture, %			Extraction into the given fraction, % of the initial amount		
		ThO_2	Ln_2O_3	U_3O_8	ThO_2	Ln_2O_3	U_3O_8
Washed thorium concentrate	1.2	68.2	31.0	0.8	99.1	7.5	28.0
Washing solution	1.2	—	—	—	—	10.9	—
Precipitate (lanthanide phosphates)	2.3	0.2	99.3	0.5	0.9	78.5	56
Precipitate enriched in uranium	6.0	—	96.7	3.3	—	3.5	16.0

The alkaline method /10, 15/

A recent method based on the decomposition of monazite concentrates with alkali solutions is now being introduced in industrial practice.

The main reaction involved in the process is:

$$(Ln)PO_4 + 3NaOH \rightarrow Ln(OH)_3 + Na_3PO_4.$$

A sufficiently high degree of decomposition of the monazite is obtained by using a finely divided concentrate (96.5% with a particle size of 0.044 mm),

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a 45% solution of NaOH at a ratio of 1.5 kg of NaOH per kg of monazite (i. e., ~ 300% excess over the stoichiometric amount) and by carrying out the decomposition for 3 hours at 140°. Increasing the processing temperature to 200° results in virtually quantitative decomposition but the hydroxide precipitates formed are sparingly soluble in acids, probably because of their partial dehydration. The main disadvantage of the use of sodium hydroxide for the decomposition of monazite is associated with the consumption of large amounts of the reagent.

Soviet scientists were able to effect a considerable reduction in the consumption of sodium hydroxide (to 150% of the stoichiometric amount) and to accelerate the process by using a ball mill heated to 130° as the reactor. The abrasive effect of the balls accelerates the reaction since it destroys the hydroxide layer formed on the grains of the mineral. Since the process combines decomposition with grinding, it does not require the use of a finely divided concentrate.

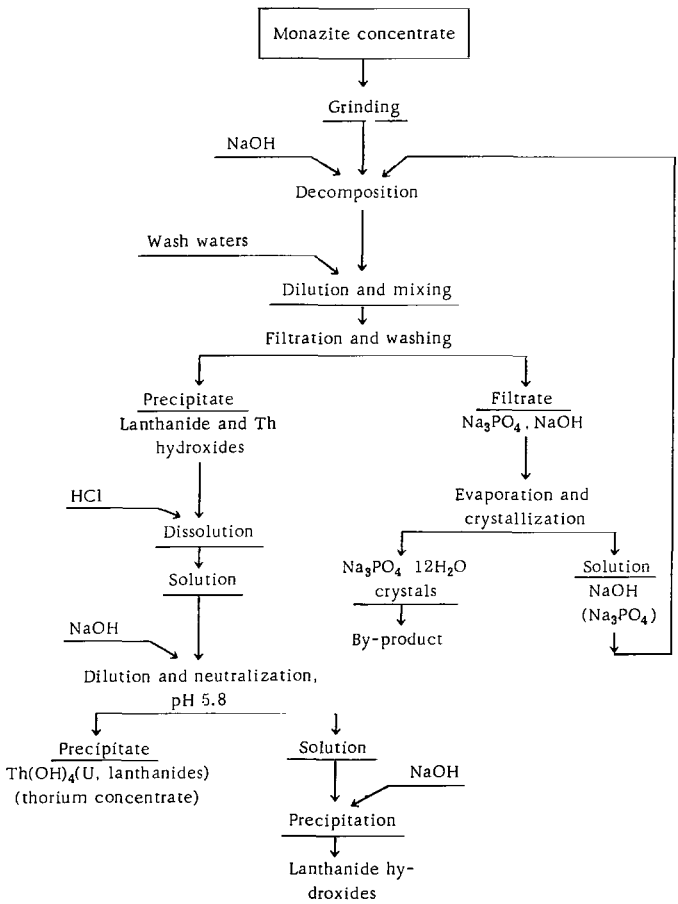

FIGURE 136. Flow sheet of the alkaline method for the processing of monazite.

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The flow sheet of the alkaline method for the processing of monazite is shown in Figure 136. The concentrate is decomposed with alkali in steel reactors. The resulting slurry is discharged into a tank in which it is diluted with the wash waters from subsequent stages (to a NaOH concentration of 30%). In order to prevent the crystallization of sodium phosphate, the slurry is heated to 100 to 110°, allowed to stand for one hour at that temperature (to obtain precipitates which are easy to separate by filtration), and is filtered while still hot. The hydrated cake is washed with water until the P_2O_5 content is reduced to 0.4% or less. The filtrate containing the Na_3PO_4 and the excess NaOH is evaporated in an evaporator and the residue is taken for the crystallization of trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) which is a valuable by-product*.

Since the solubility of Na_3PO_4 in NaOH solutions is very low (at 20° the solubility of Na_3PO_4 in 36% NaOH is only 1.3%), the major fraction of the sodium phosphate may be separated from the solution. The NaOH solution remaining from this stage is returned for the decomposition of the concentrate.

The hydroxide precipitate is dissolved in concentrated hydrochloric acid, which is taken in about 125% excess with respect to the stoichiometric amount needed for the reactions:

$$Ln(OH)_3 + 3HCl \rightarrow LnCl_3 + 3H_2O;$$

$$Th(OH)_4 + 4HCl \rightarrow ThCl_4 + 4H_2O.$$

After heating for one hour to 80° the solution is diluted with water. The insoluble residue (quartz, zircon, etc.) is separated by filtration. The resulting chloride solution is diluted and neutralized with sodium hydroxide to pH 5.8. This leads to the virtually quantitative precipitation of the thorium as thorium hydroxide. Most (99.3%) of the uranium and about 3% of the lanthanides in the solution are coprecipitated with the thorium.

The thorium concentrate is used for the preparation of pure thorium compounds and for the extraction of the uranium in it. The approximate composition of the thorium concentrate is shown below in %:

Th	36.4	Si	4.47
Lanthanides	7.45	P	0.44
U	0.74	Cl	0.36
Fe	2.21	Residue, insoluble in acids	23
Ti	6.73		

After the precipitation of the thorium, a mixture of lanthanide hydroxides is precipitated from the filtrate by the addition of alkali. The dried lanthanide hydroxide precipitate has the following approximate composition:

Lanthanides	73
Th	0.05
U	0.005
Fe	0.02
Si	0.4
P	0.1
Cl	7.9

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* Sodium phosphate is used in the production of fertilizers and in some other industries.

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As compared with the decomposition of monazite by sulfuric acid, the alkaline method has the advantage of resulting in the separation of phosphorus from the thorium and the lanthanides in the first stage of the process, and yielding a useful by-product — sodium phosphate. The disadvantages of the alkaline method include a lower degree of decomposition (even if the concentrate is very finely divided) and the consumption of large amounts of sodium hydroxide.

74. SEPARATION OF LANTHANIDES /1, 2, 7, 8, 10—13/

Because of the similarity in their properties, the separation of the lanthanides is a difficult problem.

Earlier separation methods were based mainly on the differences in the solubilities of lanthanide compounds. The individual elements, in varying degrees of purity, were prepared as a result of a large number (sometimes several thousands of successive) fractional crystallizations or fractional precipitations. The separation of some of the lanthanides was based on their oxidation to the tetravalent state (Ce, Pr, Tb) or reduction to the divalent state (Sm, Eu, Yb). In such a case the separation was facilitated because of the great difference between the properties of tetravalent or divalent lanthanides on one hand and the trivalent lanthanides on the other.

Recently the separation of the lanthanides was greatly simplified and improved by the use of ion exchange and extraction (with organic solvents) methods. These new methods do not entirely supersede the fractional crystallization and precipitation methods. Fractionation methods are, however, now only used in the initial separation stages which produce fractions enriched in individual lanthanides.

We shall briefly discuss the most common separation methods.

Fractional crystallization

Two of the widely used crystallization methods are the fractional crystallization of the double lanthanide ammonium nitrates or lanthanide magnesium nitrates (in the separation of the elements of the cerium group) and the crystallization of the bromates $LnBrO_3 \cdot 9H_2O$ (for the separation of the elements of the yttrium group). The relative solubilities of the double nitrates of the elements of the cerium group are shown in Table 50.

The solubility of the double nitrates increases from lanthanum to samarium. When the cerium is separated in advance by the oxidation method (see below), a series of fractional crystallizations of the double nitrates results in the concentration of lanthanum in the sparingly soluble fraction, of neodymium, samarium and europium in the soluble fraction, and of part of the lanthanum, praseodymium and part of the neodymium in the intermediate fractions.

The fractional crystallization is usually carried out in the sequence shown in Figure 137. The starting solution is evaporated and allowed to cool, yielding crystals and mother liquor which is separated by decantation.

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The crystals are dissolved in a fresh portion of the solvent, the solution is evaporated and the crystallization is repeated. The mother liquor from the first crystallization is subjected to a second evaporation and crystallization. The mother liquor from the second crystallization is then combined with the crystals formed after the second evaporation of the starting solution. This yields three fractions, each of which is then subjected to crystallization in a similar manner and the mother liquors and crystals from successive crystallizations are combined.

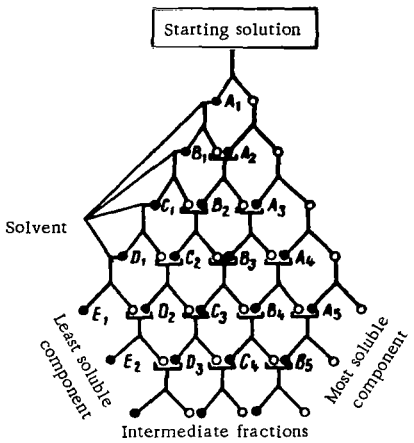

FIGURE 137. Schematic presentation of the fractional crystallization process.

— dissolution in water; ⅄ evaporation until formation of crystals; o mother liquor; ● crystals; ⌣ combined.

Each new operation increases the number of fractions in the crystallization series. When a given number of fractions is attained (usually 8 to 20), that number of fractions is subsequently maintained constant by combining the precipitates or mother liquors of the end fractions from two subsequent crystallization series or withdrawing them from the process as the end product.

TABLE 50

Relative solubilties of the double lanthanide ammonium and lanthanide magnesium nitrates (the solubility of the lanthanum salt is taken as unity)

Salt	La	Ce	Pr	Nd	Sm
$Ln(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$	1	1.5	1.7	2.2	4.6
$2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$	1	1.2	1.2	1.5	3.8

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The fractional crystallization of bromates of the elements of the yttrium group is carried out in a similar manner.

Fractional precipitation

The fractional precipitation of the double sulfates and hydroxides is most frequently used.

The precipitation of the double sulfates $(Ln)_2(SO_4)_3 \cdot Na_2SO_4 \cdot nH_2O$ is extensively used for the separation of the lanthanides into cerium and yttrium groups and occasionally into three groups:

1) cerium group (La, Ce, Pr, Nd, Sm) — sparingly soluble double sulfates;

2) terbium group (Eu, Gd, Tb, Dy) — double sulfates of intermediate solubility;

3) yttrium group (Ho, Er, Tu, Yb, Lu, Y) — soluble double sulfates.

In most cases the use of the method is confined to a rough separation into the cerium and yttrium (including terbium) groups. The precipitation is carried out from cold sulfuric or nitric acid solutions containing sodium sulfate which is added either as a solid or as a saturated solution until the disappearance of the neodymium lines from the absorption spectrum of the sample.

The separation of lanthanides by fractional precipitation of their hydroxides is based on the different pH at which the precipitation occurs (it decreases from lanthanum to lutecium, see Table 47). The solution containing the lanthanides is gradually neutralized by the addition of a dilute solution of ammonium hydroxide or by passing through the solution a stream of ammonia mixed with air (the Trombe method).

The fractions precipitated at the different pH values are separated; a fraction enriched with samarium, europium, and the yttrium earths is obtained at a low pH, followed by the intermediate fractions (Nd + Pr contaminated with La), and finally a rich lanthanum concentrate (98 to 99% La) is produced at higher ($\geqslant 8.6$) pH values.

The fractional precipitations of oxalates (for the cerium group elements) and ferrocyanides (for the yttrium group) are also used for separation.

Selective oxidation

The oxidation of cerium to the tetravalent state is the most commonly used method for its separation from the other lanthanides. Cerium is readily oxidized by oxygen on drying a mixture of lanthanide hydroxides in air at 120 to 130° or when air is passed through a hot suspension of the hydroxides. Other oxidizng agents such as chlorine or hydrogen peroxide are also used. After the oxidation of Ce^{3+} to Ce^{4+} the trivalent lanthanide hydroxides are dissolved in dilute (5 to 10%) nitric or hydrochloric acid while ceric hydroxide ($CeO_2 \cdot nH_2O$) remains in the insoluble residue. The residue contains 94 to 96% CeO_2. In order to purify the cerium concentrate residue (i. e., to remove the other lanthanides), it is dissolved in concentrated nitric acid. Pure cerium compounds are

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isolated from the solution by crystallization as cerium ammonium hexanitrate $(NH_4)_2Ce(NO_3)_6$ or by precipitation as the basic cerium nitrate $Ce(OH)_x \cdot (NO_3)_{4-x}$ which is formed when the solution is diluted and neutralized to pH $\approx$ 0.7 to 1.

Another method which is extensively used for the purification of cerium is the selective extraction of $Ce(NO_3)_4$ from 6 to 8 N nitric acid by diethyl ether or tributyl phosphate (see below).

Selective reduction

Reduction to the divalent state is used for the isolation of samarium, europium, and ytterbium from fractions enriched in these elements. The properties of the divalent samarium, europium, and ytterbium resemble the properties of the alkaline-earth elements and in particular those of strontium and barium. Thus, in contrast to the sulfates of the trivalent lanthanides, their sulfates are sparingly soluble. The commonly used reducing agent is sodium amalgam which is mixed with an acetate solution of the lanthanide mixture to be separated:

$$Ln(CH_3COO)_3 + 2Na(Hg) = Ln(Hg) + 3CH_3COONa.$$

The reduced elements are extracted from the amalgam by hydrochloric acid.

Samarium and europium are separated by selective reduction of Eu^{3+} to Eu^{2+} with zinc amalgam or zinc dust, which do not reduce Sm^{3+} to Sm^{2+}. This can be attributed to the different values of the oxidation-reduction potentials of samarium and europium.

The oxidation-reduction potentials of the lanthanides (with respect to hydrogen electrode) are (volts):

$La = La^{3+} + 3\bar{e}$	−2.37
$Y = Y^{3+} + 3\bar{e}$	−2.1
$Pr = Pr^{3+} + 3\bar{e}$	−2.0
$Sm^{2+} = Sm^{3+} + \bar{e}$	−1.72
$Yb^{2+} = Yb^{3+} + \bar{e}$	−1.15
$Eu^{2+} = Eu^{3+} + \bar{e}$	−0.43
$Pr^{3+} = Pr^{4+} + \bar{e}$	+1.60
$Ce^{3+} = Ce^{4+} + \bar{e}$	+1.61

The hydrochloric acid solution containing Sm^{3+} and Eu^{3+} is passed through a column packed with granulated zinc amalgam. The solution is collected in dilute sulfuric acid when europium sulfate $EuSO_4$ is precipitated.

Selective reduction of europium (as a means for its separation from samarium and the other lanthanides) may also be accomplished by electrolysis using a mercury cathode. The electrolysis is carried out in acetate solution containing potassium citrate. The potassium citrate and the lanthanides form complexes of $K_3[Ln(C_6O_5H_7)_2]$ type which are so stable that no precipitation of lanthanide hydroxides occurs when the solutions are alkalized to pH 7 to 9. (i. e., the pH at which the electrolysis is carried out). A diagram of the electrolytic cell used for the reduction is shown in Figure 138. After the separation of europium the amalgam is washed with

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water (to remove potassium, a part of which is also separated) and europium is then extracted with hydrochloric acid.

Another variant of the separation of samarium from europium consists in the selective oxidation of a mixture of the divalent sulfates of these elements with nitric acid: samarium is more readily oxidized and is extracted into solution.

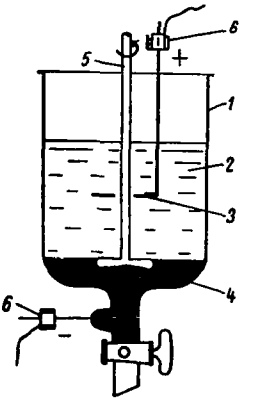

FIGURE 138. Diagram of an electrolytic cell for the reduction of europium on a mercury cathode.

1— glass vessel; 2— electrolyte; 3— platinum leaf anode; 4— mercury cathode; 5— stirrer; 6— terminals.

Separation with ion exchange resins

Ion exchangers are sparingly soluble solids (organic or inorganic) with active (ionogenic) groups which can be exchanged for ions present in solution.

The most important ion-exchanging materials are the synthetic organic resins which are extensively used, in particular, in extractive metallurgy of nonferrous and rare metals (for the extraction of ions from dilute solutions) and for the purification and separation of elements with similar properties. The modern synthetic ion exchangers (organic resins) are very large, interconnected molecular chains (cross-linked polymers); they form an insoluble three-dimensional lattice which swells in water. Active groups, which are capable of undergoing electrolytic dissociation, are "suspended" on the polymer chains. Ion exchangers are subdivided into two groups.

Cation exchange resins consist of an insoluble acid anion of high molecular weight and contain active groups (mostly SO_3H or COOH) which can exchange a hydrogen ion for a cation present in the solution.

Anion exchange resins consist of an insoluble cation (base) of high molecular weight and labile, exchangeable anions. The most common active groups in anion exchange resins are the amino groups ($-NH_2$, $=NH$, $\equiv N$).

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Cation and anion exchange resins are produced commercially in the form of granulated materials of various particle sizes.

Like the conventional chemical reactions, the ion exchange process, obeys the Law of Mass Action and is characterized by the ion exchange constant. Thus, the reaction on cation exchange resins can be expressed by the equation:

$$RM_1 + M_2 \rightleftarrows RM_2 + M_1,$$

where M_1 and M_2 are the cations to be exchanged, and R is the insoluble anion in the cation exchange resin.

For a reaction involving exchange of cations of the same valency, the ion exchange equilibrium may be expressed as follows, in accordance with the Law of Mass Action:

$$\frac{C_1}{C_2} = K\frac{N_1}{N_2},$$

where C_1 and C_2 are the concentrations of M_1 and M_2 in the solution, N_1 and N_2 are the respective concentrations on the resin, and K is the ion exchange constant. The equation for the exchange of ions of different valencies assumes the form:

$$\frac{C_1^{Z_2}}{C_2^{Z_1}} = K\frac{N_1^{Z_2}}{N_2^{Z_1}},$$

where Z_1 and Z_2 are the valencies of the ions.

Cation and anion exchange resins may be "charged" with different cations and anions. It is thus accepted practice to speak about cation exchange resins in the H^+, Na^+, NH_4^+-forms, etc., and pf anion exchange resins in the SO_4^{2-}, OH^-, Cl^- and other forms.

The ion exchange may be carried out under static or dynamic conditions. In the static method all the solution containing the ion to be exchanged is brought into contact (by stirring) with a certain amount of the resin, and the resin is then separated from the solution by filtration. The method is not very effective, especially in the case of low ion exchange constants when a large number of repeated operations is required. In the dynamic method (which is the one most frequently used) the solution is passed through a column packed with the resin. In such a case the resin is first saturated completely in the upper layers and subsequently in the lower layers.

Ion exchange resins are characterized by their sorption capacity (for a given ion under certain defined conditions). The sorption capacity is expressed either in gram-equivalents per gram of resin or in percent of the weight of the resin.

The sorption capacity of the resin depends on a number of factors: the value of the ion exchange constant, the filtration rate, the concentration and nature of the ions to be exchanged, the grain size of the resin, the pH of the solution. When operating under dynamic conditions distinction is made between: a) the working sorption capacity, i. e., the amount of substance absorbed by the resin until the "breakthrough" (the appearance of the absorbed ion in the filtrate); b) the total sorption capacity, i. e., the amount of substance absorbed before complete saturation of the resin

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takes place. The resin capacity is usually determined from the efflux curves which show the dependence of the concentration of the exchanged ion in the filtrate as a function of the volume of the solution passed (Figure 139). The volume of filtrate prior to the "breakthrough" (section "a") is a measure of the working sorption capacity of the resin. The area S_1 corresponds to the total amount of the ion absorbed in the resin prior to the "breakthrough", while the total area bounded by the discharge curve is a measure of the total capacity of the resin. The ion exchange includes the following stages:

1) sorption of ion from solution; the filtration of the solution through the resin bed is continued either to "breakthrough" or to complete saturation of the resin;

2) washing the resin with water;

3) elution of the sorbed ion and regeneration of resin.

In most cases the elution is carried out with solutions containing ions with which the resin must be "charged" for the sorption cycle. The elution curve has the shape shown in Figure 140. During the elution the concentration of the ion in the filtrate first increases rapidly and then decreases just as rapidly. When the sorption is carried out from solutions with a low concentration of the ion to be extracted, the sorption-elution cycle yields solutions in which the concentration of the ion is 10 to 100 times higher than in the starting solution.

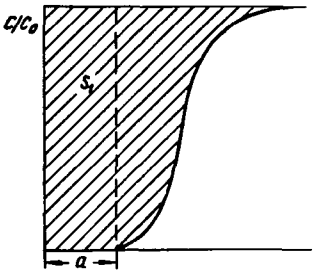

FIGURE 139. Efflux curve for sorption on resin under dynamic conditions.

a — volume of solution passed prior to the "breakthrough"; S_1 — area numerically equal to the working sorption capacity of the resin (prior to the "breakthrough"); C/C_0 — ratio of the ion concentration in the filtrate to its initial concentration.

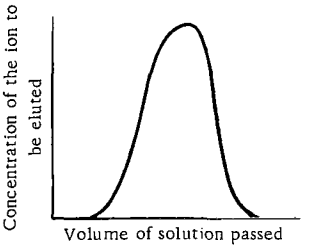

FIGURE 140. Typical elution curve.

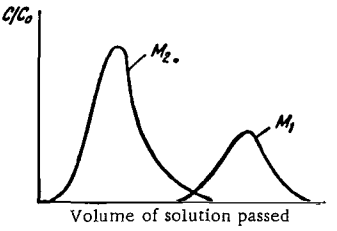

FIGURE 141. Elution curves for two ions (M_1 and M_2) sorbed on a resin.

The different ions differ in their affinity for the resin, which depends mainly on the ionic charge and the size of the hydrated ion. This is the principle of the separation of ions by the ion exchange method.

The separation of ions of elements with similar properties (e.g., zirconium and hafnium, tantalum and niobium, lanthanide elements) is

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best carried out by the so-called ion exchange chromatography*. The mixture of ions to be separated is first sorbed in the upper part of the resin charge in a column. The ions are then eluted from the saturated layer. Depending on their affinity for the resin, the ions in the mixture are separated during the elution into individual zones which move along the column at definite rates. The zone containing the ions with the lowest affinity for the resin will have the highest rate of motion.

The separation of ions M_1 and M_2 (if the affinity of M_1 for the resin is higher than that of M_2) would yield an elution curve such as that shown in Figure 141, in which each of the two curves corresponds to a sorption band containing one of the ions. At the exit of the column the filtrate fractions containing M_1 and M_2 ions are collected separately. Theoretically, each zone should contain the ions of only one of the elements to be separated. In practice, however, the zones are superimposed (the extremities of the elution curves often spread out) which makes quantitative separation difficult.

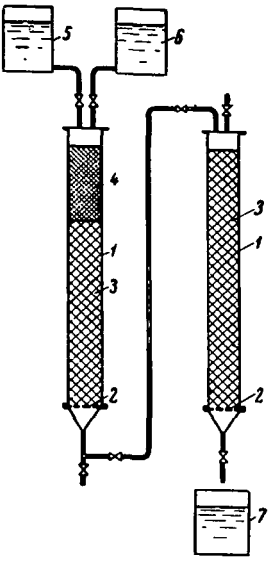

FIGURE 142. Diagram of an installation for the separation of elements by ion exchange.

1—column; 2—grid; 3—ion exchange resin; 4—upper layer of the resin, with the mixture of elements to be separated sorbed on it; 5—pressurized vessel with the solution containing the elements to be separated; 6—vessel with the eluent; 7—collection vessel for the filtrate.

The separation of ions with similar properties may be made more efficient by using eluent solutions containing some complex-forming agent which binds the ions to be separated into complex compounds of various degrees of stability.

Ion exchange processes are carried out in cylindrical columns charged with the granulated resin. A draining system (grid) which allows the solution which has passed through the resin bed to be tapped without entrainment of resin particles is fitted to the lower part of the filter (see Figure 142).

Various types of cation exchange resins are used for the separation of lanthanides by ion exchange (the resin used in the USSR is KU-2, in the USA Dowex 50 and others). These resins are strongly acid cation exchange resins produced by copolymerization of styrene and divinylbenzene and containing SO_3H as the active group.

The affinity of the lanthanides for the resin decreases from La^{3+} to Lu^{3+}, i.e., as the size of the hydrated ions is reduced. However, the affinities of the various lanthanides for the resin differ only very slightly and the separation is not entirely satisfactory. Better separation is obtained by eluting with solutions containing

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* The chromatographic method was developed by the Russian botanist Tsvet in 1903, who intended to use it for the separation of plant pigments. The term "chromatographic adsorption" was proposed by Tsvet on account of the colored adsorption bands which were produced on the adsorbent during the separation.

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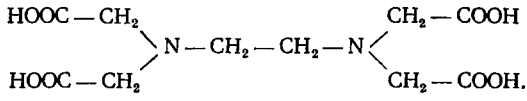
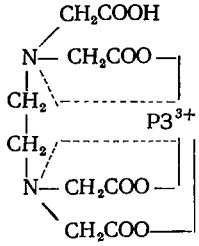
organic compounds which form complexes of different degrees of stability with the lanthanides.

The order of the elution corresponds to the relative strength of the anionic lanthanide complexes. As the eluent moves along the column (or a number of columns connected in series) the mixture of cations is separated into sorption zones (bands) which move at certain definite velocities. Various organic compounds which form lanthanide complexes are used for the elution: citric acid, nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA). EDTA is the eluent most widely used in the chromatographic separation of the lanthanides. It is an α-amino acid. EDTA is a tetrabasic acid with two nitrogen atoms:



Trivalent lanthanides form chelate complexes with EDTA in which the nitrogen atoms are bound to the lanthanide ions by coordination bonds:



The stability constant of these complexes is given by the equation:

$$(HEDTA)^{3-} + Ln^{3+} \rightleftharpoons H(LnEDTA)$$

$$K = \frac{[H(LnEDTA)]}{[Ln^{3+}]\,[HEDTA^{3-}]}$$

As is evident from Figure 143, the stability constants of the lanthanide complexes with EDTA increase from La to Lu, i. e., with the atomic number of the element. The stability constants of the complexes of two adjacent lanthanides differ on the average by a factor of 2.4. This explains the high selectivity of EDTA as an eluent of the lanthanide cations from the resin.

The lanthanides are separated by using a system of several columns charged with the resin and connected in series. The first few columns in the system serve for the saturation of the resin with the lanthanides while the remaining columns are separatory. During elution individual sorption zones are formed in these columns.

In the saturation columns the resin is first charged with NH_4^+ or Na^+ ions (i. e., the resin is used in the NH_4^+ or Na^+ form). The resin in the separatory columns is in the Cu^{2+} form. The Cu^{2+} ions serve as retarders

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which improve the separation. The copper complex with EDTA is more stable than the complexes of most of the lanthanides with EDTA (see Figure 143). Thus, when the eluent containing the complex lanthanide-EDTA ions is passed through the separatory column, the copper ions pass into solution and displace the lanthanide ions from the solution into the resin, thus retarding their motion. The lanthanide ions are displaced from the solution on to the resin in an order corresponding to the strength of their complexes with EDTA, which results in the formation of better defined sorption zones.

Usually the pH of the eluent is adjusted to 4 to 8.5 (depending on the operating conditions) by neutralization with ammonium hydroxide. Thus, the eluent contains the ammonium salt of EDTA. A dilute solution of EDTA (0.5 to 1%) is used as the eluent since the ammonium salts of the lanthanide-EDTA complex acid (NH_4(LnEDTA) nH_2O) and the copper complex Cu_2(EDTA) · $5H_2O$ are not very soluble. The use of more concentrated solutions causes the precipitation of salts which clog the pores between the resin grains and thus interfer with the normal operation. The low EDTA concentration in the eluent limits the output of the separation process since the lanthanide concentration in the filtrate is low.

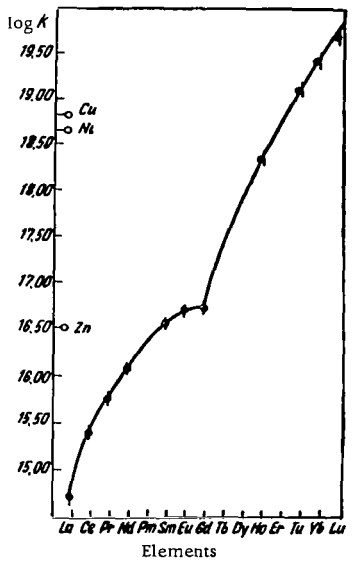

FIGURE 143. Dependence of log K on the atomic number of the lanthanides (K is the stability constant of the lanthanide-EDTA complex).

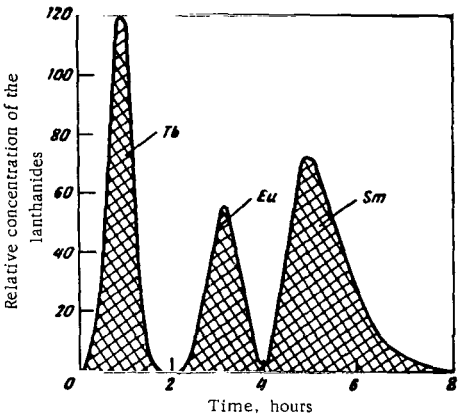

FIGURE 144. Elution curves of terbium, europium, and samarium sorbed on the resin by a 0.26 M solution of EDTA, at pH = 3.62.

The filtrate fractions are collected separately at the issue from the column system. The first filtrate contains only copper ions. Fractions containing lanthanide ions appear only later as the copper is eluted from the system; the order of elution of the lanthanides is determined by the

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stability of their EDTA complexes. Figure 144 gives the elution curves (with EDTA solutions) for the separation of three elements. The first wave corresponds to the elution of terbium, the second to europium, and the third to samarium, in accordance with the decreasing complex strength in sequence Tb — Eu — Sm.

The EDTA solutions are regenerated by acidification to pH 0.5 to 1. This causes the decomposition of the lanthanide complexes and the precipitation of the sparingly soluble EDTA.

If the initial specific charge on the column* with the lanthanide mixture is small (less than 5% on the weight of the resin) and the total length of the separatory columns is large enough, each filtrate fraction at the issue from the last column contains only one of the elements to be separated.

The chromatographic method may be used to prepare individual lanthanides of a high degree of purity, but the yields are low. Accordingly, in most cases the elements are preliminarily separated by some other method and the ion exchange method is used only for the separation and purification of like elements.

Extraction

The separation of the lanthanides by extraction is based on the different distribution coefficients of the lanthanides between their aqueous solutions and organic solvents (see Chapter 3, p. 122).

The extractant most widely used for the separation of the lanthanides is TBP, which has been described above. Lanthanide nitrates and TBP form complexes of the $Ln(NO_3)_3 \cdot 3TBP$ type.

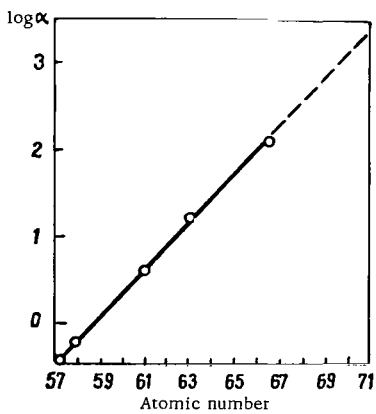

FIGURE 145. Effect of the atomic number on the distribution coefficients of lanthanide nitrates between aqueous phase and TBP (HNO_3 concentration — 15.6 M)

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* The specific charge is the ratio of the weight of the ions sorbed on the resin to the total weight of the resin.

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When lanthanide nitrates are extracted by TBP from solutions in which the HNO_3 concentration is above 5 M the distribution coefficients steadily increase with the atomic number of the element (Figure 145). The separation coefficients $\beta = \frac{\alpha_{Z+1}}{\alpha_Z}$ for two adjacent elements depend on the nitric acid concentration*. Thus, for Z-values between 57 (lanthanum) and 64 (gadolinium) the separation coefficients are 1.9 and 1.6 for solutions with nitric acid concentrations of 15.6 and 12 M respectively. The nitric acid concentration may be reduced without decreasing the value of β by adding to the solution certain nitrates ($Al(NO_3)_3$, $LiNO_3$) which act as salting-out agents, i. e., which displace the lanthanide nitrates into the organic phase. The separation coefficients for adjacent elements in the yttrium group ($Z = 64-71$) are lower than in the cerium group. Hence, their separation by extraction is more difficult than the separation of elements in the cerium group.

The distribution coefficients increase with increasing concentration of the lanthanide in the solution; this makes it advantageous to process large amounts of lanthanides.

Two extraction methods are used for separation purposes:

1) in countercurrent in column extractors or a series of mixer-settler extractors, with the aqueous and organic phases moving continuously in countercurrent (see Figure 66);

2) in semi-countercurrent in which the aqueous phase is stationary while the organic phase is in motion and the mixture to be separated is added at the beginning to the first extractor (Figure 146).

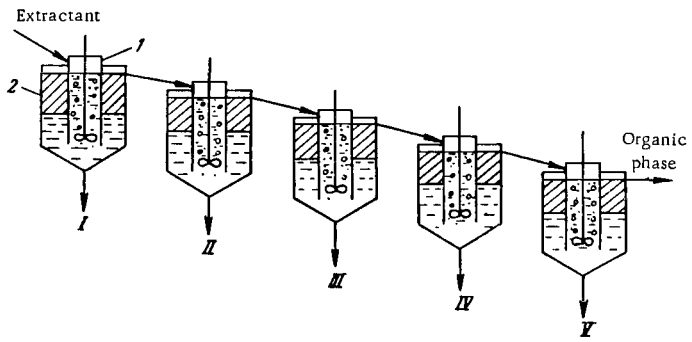

FIGURE 146. Diagram of semi-countercurrent extraction.

1 — mixing chamber; 2 — settler; I, II, III, IV, V — aqueous fractions.

When using the first method the starting mixture of the lanthanides is separated into two fractions. Since the separation involves not two, but a large number of elements, the process must be repeated many times (i. e., multistage extraction is required) and the number of separations must be at least $n-1$, where n is the number of elements to be separated. However, the process has the advantage of being completely continuous, which is to be preferred for the separation of large quantities.

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* α_{Z+1} and α_Z are the distribution coefficients for elements with atomic numbers Z+1 and Z respectively.

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In semi-countercurrent extraction the starting mixture of elements to be separated is introduced into the first extractor and the remaining extractors are filled with a solution of nitric acid (or a solution containing nitric acid and the salting-out agent). The organic phase (TBP) is then fed into the system and passes successively through all the extractors. The contact between the aqueous and organic phases in each extractor results in the establishment of an equilibrium distribution of the elements between the two phases. Elements with lower atomic numbers concentrate in the first extractors while elements with higher atomic numbers concentrate in the last extractors. Thus, a single passage of the extractant leads to the separation of the lanthanide mixture into a number of fractions. The technique is convenient when separation of small quantities is involved. Both undiluted TBP and solutions with a high concentration of lanthanide nitrates (100—200 g/l of Ln_2O_3) are viscous. Thus, it is recommended that extractors of the mizer-settler type be used.

The extractive separation method has a high output and its use is increasingly frequent.

Separation scheme

Various separation schemes which combine the methods described above are used at present. As an illustrative example, a scheme showing the order of separation of elements of the cerium group is given in Figure 147.

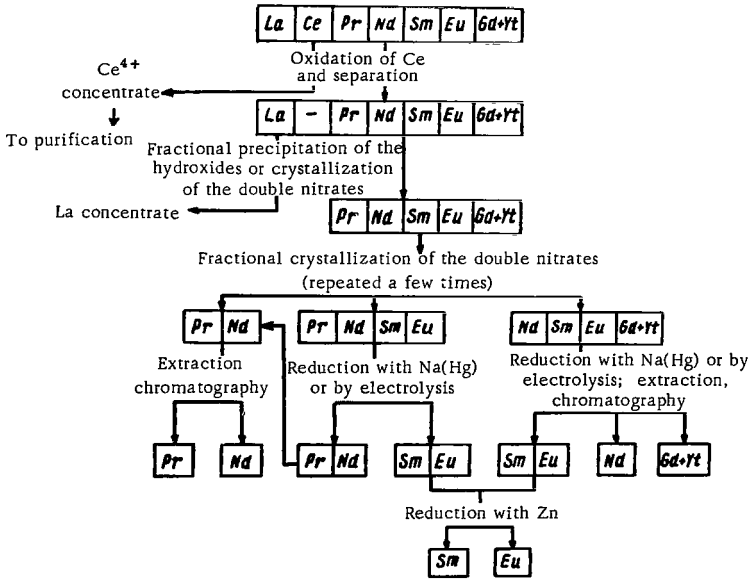

FIGURE 147. Sequence of separation of elements of the cerium group (Yt — elements of the yttrium group).

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The mixture taken for the separation usually contains hydroxides and is free of contaminants. The cerium is separated first, by oxidation (see p. 281). After the separation of the cerium, lanthanum concentrate is isolated from the nitrate (occasionally chloride) solution by fractional concentration of the hydroxides or fractional crystallization of the double ammonium nitrates. The remaining elements are subjected to a rough separation into several fractions by fractional crystallization of the double nitrates. Neodymium and praseodymium are then separated by extraction and by the chromatographic method.

Samarium and europium are isolated and separated from the intermediate samarium-europium fraction by the reduction method (see p. 281). The elements of the third fraction are separated by reduction, extraction and ion exchange.

The above scheme still includes fractional crystallization as a means of rough separation. In more modern schemes extractive methods are used for the separation into fractions.

75. CONTROL OF SEPARATION AND PURITY OF LANTHANIDE COMPOUNDS

Because of the similarity in the chemical properties of the lanthanides, the conventional analytical methods (volumetric or gravimetric) cannot be used to determine the composition of a lanthanide mixture. The only exceptions are cerium, which can be determined by a number of methods based on its oxidation to the tetravalent state, and europium, which can be reduced with relative ease to the divalent state. Thus, the analysis of the lanthanides is carried out with the aid of physical methods. These include: magnetic methods (measurements of the magnetic susceptibility), spectroscopic methods (absorption, arc, spark, and X-ray spectra), the chromatographic method, and the radiometric method.

The measurement of the magnetic susceptibility is extensively used for the control of the separation of the elements during fractionation. It has the advantages of being a rapid method and of permitting the use of preparations in any form (solutions, solid substances).

The lanthanides and their compounds are paramagnetic. Their interaction with an external magnetic* field draws them into the field. The magnetic permeability (and the molar magnetic susceptibility which is related to it) is measured with the aid of a magnetic balance. A curve showing the magnetic moments of the lanthanides as a function of their atomic numbers is given in Figure 130. The magnetic susceptibilities are strictly additive. Thus, the composition of a binary mixture of lanthanides may be determined with an accuracy of 2—3% if the magnetic susceptibility of each of the components is known.

Spectroscopic methods are more accurate and offer more scope. The method most widely used for the determination of the degree of separation and purity of the lanthanide elements is adsorption spectrophotometry. The absorption spectra of the lanthanides have been shown in Figure 133. By using modern photoelectric spectrophotometers, large amounts of most lanthanides can be determined with an accuracy of ± 1.5%. However, the bands are not intense enough for the determination of small amounts of contaminants.

Spectroscopy in the arc and especially X-ray spectroscopic methods are the most sensitive. At present, X-ray spectroscopic analysis is one of the most accurate methods for the determination of the composition of a mixture of lanthanides.

The radiometric method (introduction of different radio-isotopes of lanthanides at various stages of the process) is extensively employed to follow the separation of the lanthanides. This method is especially effective in the chromatographic separation of the elements.

The determination of the mean atomic weight may be used as a simple method for the evaluation of the composition of binary lanthanide mixtures. The mean atomic weight is calculated from the oxide-to-oxalate ratio. The oxide content is determined by igniting a weighed amount of the dry oxalate to constant weight, while the oxalate content is determined by dissolving the salt in sulfuric acid and titrating with permanganate solution. The determination of the mean atomic weight is especially valuable in the control of the separation of yttrium-containing systems since its atomic weight differs sharply from the atomic weights of the lanthanides.

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* Lanthanum is diamagnetic.

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76. MANUFACTURE OF RARE-EARTH METALS /9, 10, 12/

Because of the high chemical stability of the lanthanide compounds (oxides, halides), the pure metals and their alloys are produced by thermal reduction with metals or by the electrolysis of molten salts.

Starting compounds for the manufacture of metals

Metallic lanthanides are produced mainly from anhydrous lanthanide chlorides or fluorides.

Lanthanide **chlorides** are prepared by the action of various chlorinating agents on lanthanide oxides; chlorine (in the presence of carbon), carbon tetrachloride, sulfur chlorides, ammonium chloride and hydrogen chloride are used as the chlorinating agents.

The chlorination of oxides by chlorine in the presence of carbon results in the contamination of the chlorides produced with carbon since lanthanide chlorides do not distil under the process conditions used (600 to 800°) and contain the excess carbon added to the starting mixture.

Carbon tetrachloride* reacts with lanthanide oxides at 700 to 800°:

$$2(Ln)_2O_3 + 3CCl_4 \rightarrow 4(Ln)Cl_3 + 3CO_2$$

(some CO and $COCl_2$ are also formed).

The chloride produced by the above method contains only a very small amount of carbon. This is explained by the dissociation of some CCl_4 at high temperatures:

$$2CCl_4 \rightleftarrows Cl_2 + C_2Cl_6,$$
$$C_2Cl_6 \rightleftarrows 3Cl_2 + 2C.$$

The chlorination with chlorine or CCl_4 vapors is carried out most conveniently in shaft furnaces charged with the pelletized material (the pellets contain a mixture of the oxides with carbon when chlorine is used as the chlorinating agent, or pelletized oxides when using CCl_4). As is evident from Table 46, the chlorides of most lanthanides melt within the range 700 to 850°. Thus, chlorination at 800 to 850° yields a mixture of the molten chlorides which can be discharged periodically from the furnace.

Chlorides of a higher degree of purity are produced in the chlorination of lanthanide oxides by sulfur chloride, hydrogen chloride or ammonium chloride; the reactions involved are:

$$2(Ln)_2O_3 + 6S_2Cl_2 \rightarrow 4(Ln)Cl_3 + 3SO_2 + 9S;$$
$$(Ln)_2O_3 + 6HCl \rightarrow 2(Ln)Cl_3 + 3H_2O;$$
$$(Ln)_2O_3 + 6NH_4Cl \rightarrow 2(Ln)Cl_3 + 6NH_3 + 3H_2O.$$

The simplest process is the one based on the use of ammonium chloride. In this process a mixture of the lanthanide oxides and NH_4Cl (in ~ 100% excess over the stoichiometric amount needed) is heated at 200 to 300° until a sample withdrawn from the reaction mixture proves

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* Carbon tetrachloride is a nonflammable liquid boiling at 78°.

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to be fully soluble in water. The excess NH_4Cl is then expelled by heating the chloride to 300 to 320° in vacuo (0.5 to 2 mm Hg). The elimination of ammonium chloride must be quantitative to prevent contamination of the lanthanides by nitrogen.

Since the anhydrous lanthanide chlorides are very hygroscopic, they must be transferred rapidly from one container to another when hot and out of contact with humid air. It is best to store the chlorides in an inert gas.

Anhydrous lanthanide fluorides may be prepared by dehydration of the hydrates precipitated from solution or by the action of hydrogen fluoride or ammonium bifluoride on lanthanide oxides.

Dehydration of fluoride hydrates. Lanthanide fluorides are sparingly soluble and are precipitated quantitatively from chloride, sulfate and nitrate solutions by the addition of hydrofluoric acid. They are precipitated either as the hydrated fluorides of the $LnF_3 \cdot 0.5H_2O$ type (La, Ce, and other fluorides) or as the anhydrous fluorides (Pr and Nd).

When a solution containing the fluoride precipitates is heated under an infrared lamp, the hydrated fluorides are converted into the anhydrous form. The precipitates are then separated by filtration, washed with alcohol, and dehydrated further by heating to 400° in a dry inert gas atmosphere (argon) under reduced pressure (about 100 mm Hg). The fluorides prepared by the above method are still contaminated with the oxyfluorides LnOF. The formation of the oxyfluorides may be prevented by drying in a stream of hydrogen fluoride.

Fluorination of oxides. Fluorides of a higher degree of purity, which are not contaminated with oxyfluorides, are produced by the action of gaseous hydrogen fluoride on the oxides:

$$(Ln)_2O_3 + 6HF \rightarrow 2(Ln)F_3 + 3H_2O.$$

A rapid reaction takes place at 550 to 575°. The process may be carried out in nickel or nickel-copper (70% Ni, 30% Cu) tubes in which the boats with the oxides move in a direction opposite to the direction of the gas flow. At 500 to 600° the rate of attack of dry hydrogen fluoride on nickel is very low (about 0.9 mm/year) because of the formation of a protective film of nickel fluoride. Graphite boats may be used. Hydrogen fluoride is fed into the tube from steel tanks. The unreacted gas at the issue from the tube may be absorbed either in a sodium carbonate solution or in condensers cooled with dry ice (solid CO_2) and returned to the fluorination process.

Ammonium bifluoride NH_4HF_2 may be used as the fluorinating agent instead of hydrogen fluoride. Lanthanide oxides are fused with ammonium bifluoride at 200°:

$$(Ln)_2O_3 + 6NH_4HF_2 \rightarrow 2(Ln)F_3 + 3H_2O + 6NH_4F.$$

The excess ammonium bifluoride and ammonium fluoride are then expelled by distillation at 450°. The process yields a fluoride with a composition similar to that of the fluoride produced by fluorination with gaseous HF. However, ammonium fluoride must be quantitatively removed in order to prevent contamination of the metals with nitrogen. Since this is rather difficult, it is best to prepare lanthanide fluorides by fluorination with hydrogen fluoride.

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In contrast with lanthanide chlorides, lanthanide fluorides are not very hygroscopic. However, they can absorb gases from air. Hence, it is recommended that they be stored in an inert gas atmosphere.

Materials for the smelting of the rare-earth metals

The purity of the metals thus produced depends on the impurity content of the starting materials and of the crucible material used for the smelting of the metals and of the electrodes (when electrolytic methods are used).

The data in Table 51 show the resistance of various refractory materials and metals to the action of molten lanthanides. Of the oxides, electrically fused magnesium oxide and beryllium oxide possess a satisfactory resistance up to 1200°. Tantalum is the most resistant of the refractory metals, and may be used for melting lanthanides at temperatures up to 1700°. Molybdenum is also quite resistant, and is frequently used as the cathode in the electrolytic production of rare-earth metals.

TABLE 51

Interaction of lanthanides with various electrode and crucible materials

Material	Behavior
MgO	Not attacked up to 1200°.
CaO	Not attacked up to 1000°.
BeO	Not attacked up to 1250°.
Al_2O_3, ZrO_2, ThO_2, SiO_2	React with molten lanthanides.
Tantalum	Does not react with the metals in vacuo or in inert gases at temperatures up to 1700°. Not attacked by molten lanthanide halides.
Molybdenum	Does not react in vacuo or in inert gases at up to 1400°. Not attacked by molten halides.
Tungsten	Attacked slowly by the molten metals, not attacked by the molten halides.
Copper, nickel, iron	React with the molten metals at various rates, depending on the temperature. Cast iron may be used to construct electrolytic baths for the production of technical grade mischmetall and cerium.
CaF_2 (fluorite)	Not attacked at low temperatures (800 to 900°), rapidly attacked at high temperatures.
Graphite	Reacts slowly with molten metals, not attacked by molten halides
Porcelain	Rapidly attacked.

Graphite is used both as an electrode and as crucible material; however, the metals which are produced in contact with graphite are always contaminated with carbon since graphite reacts slowly with molten lanthanides.

Electrolytic production of rare-earth metals /10/

There are various methods for the production of lanthanides by the electrolysis of molten salts. Those most widely used are based on the

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electrolysis of anhydrous lanthanide chlorides dissolved in molten alkali or alkaline-earth chlorides. This method is used for the production of commercial quantities of mischmetall, cerium, lanthanum, neodymium, and other metals of the cerium group. During the electrolysis the molten metals are deposited on the cathode since their melting points are relatively low.

The electrolytic production of metals of the yttrium group (with the exception of ytterbium) which have high melting points (1350 to 1700°) is more difficult. Electrolysis which would deposit the molten metals on the cathode is virtually impossible at such temperatures, because of the vaporization of the halides and the difficulties associated with the selection of bath and electrode materials. In order to obtain these metals in a liquid state without raising the bath temperature above 1100° the electrolysis is carried out with liquid cadmium or zinc cathodes and the lanthanides are obtained as an alloy with the cathodic metal. The rare-earth metals are then separated from zinc or cadmium by vacuum distillation of the latter. This method has been used on a laboratory scale for the production of lanthanum, samarium, gadolinium, europium, and dysprosium.

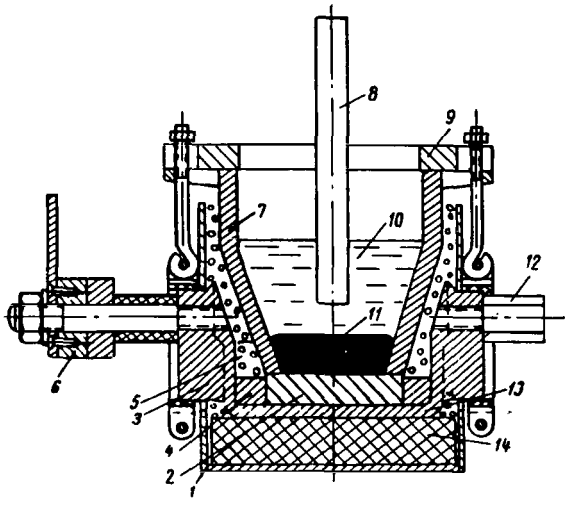

FIGURE 148. Diagram of an electrolyzer for the production of technical cerium or mischmetall (an alloy of the lanthanides of the cerium group).

1—steel body; 2—graphite cathode; 3—cast-iron body; 4—graphite packing; 5—crushed chamotte packing; 6—current lead to the cathode; 7—graphite crucible; 8—graphite anode; 9—cast-iron ring; 10—molten electrolyte; 11—molten metal; 12—pivots for rotating the electrolyzer; 13—cast-iron crucible; 14—chamotte lining.

In most cases the electrolytes used are based on an eutectic mixture containing 50% KCl + 50% $CaCl_2$ (mp 660°) or a mixture containing 50% KCl + 50% NaCl (mp 658°). Lanthanide chlorides are quite soluble in these

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molten mixtures. The bath contains about 58 to 60% $LnCl_3$ and the rest consists of the alkali and alkaline-earth chlorides. The addition of small amounts of calcium fluoride is recommended.

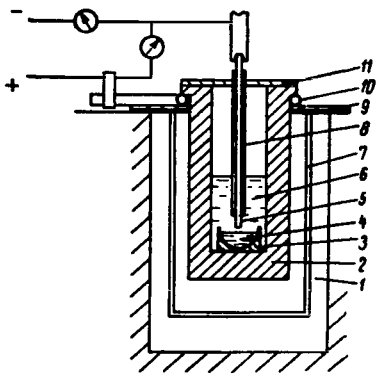

FIGURE 149. Diagram of an electrolyzer for the production of pure rare-earth metals.

1—furnace; 2—graphite crucible (anode); 3—beryllium oxide crucible; 4—molten cerium; 5—molybdenum cathode; 6—electrolyte; 7—nickel crucible; 8—tubular quartz shield; 9—asbestos gasket; 10—water-cooled copper tube connecting the anode to the current; 11—graphite cover.

An electrolyzer used in Germany for the production of technical grade mischmetall /10/ is shown in Figure 148. It consists of a graphite crucible (serving as the cathode) on a graphite bottom plate placed in a cast-iron body. The body is fitted with pivots which permit the bath to be rotated. The electrical current is supplied to the body, which is in electrical contact with the graphite plate, by means of a packed layer of graphite and pitch. The graphite crucible is fastened to the bottom plate with the aid of a cast-iron ring. The cast-iron body together with the crucible are mounted within an iron jacket. The space between the jacket and the crucible is packed with crushed chamotte and the bottom is lined with chamotte bricks. The bath volume is 30 liters. A lifting graphite anode 100 mm in diameter is fitted in the center of the bath.

At first the electrolyte is fused by passing current through the graphite rod placed between the electrodes. The rod is then removed and the bath is maintained in a molten state by the heat evolved in the passage of the current through the melt. Additional batches of the charge are periodically fed into the electrolyte and the process is continued until the crucible has been filled. The concentration of oxychlorides LnOCl (which are formed by the interaction of lanthanide chlorides with moisture from the air) in the lanthanide chlorides taken for electrolysis must be as low as possible. The oxychlorides are not decomposed by the current, but their presence in the melt causes partial precipitation of the metal on the cathode in a finely dispersed state (as a "mist"). The fine metallic particles float to the surface of the bath and are oxidized if the electrolysis is carried out in the presence of air. When the finely dispersed metal particles reach the anode they are chlorinated, yielding chlorides which dissolve in the melt. The appearance of these finely dispersed particles results in a sharp decrease in the current efficiency. The deposition of the metal in a finely dispersed state is also observed at very high or very low current densities.

The electrolysis is carried out at a potential of 12 to 15 V and a current of 2000 to 2200 amp (for a 30 liter crucible) which corresponds to a cathodic current density of ~ 3 amp/cm^2. The current efficiency is about 60 to 70%. The bath temperature is 900 to 1100°. During the electrolysis, chlorine is evolved at the anode. Hence, the bath must have a satisfactory exhaust system. After the crucible has been filled the bath is tilted and its

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contents are poured into steel pans preheated to 500 to 550°. During the pouring the metal is protected against oxidation by the molten salt.

The mischmetall or cerium produced by the electrolysis contains 94 to 99% lanthanide elements and a series of impurities: carbon, calcium, aluminum, up to 1% silicon, 1 to 2.5% iron, etc. A metal of a higher degree of purity may be produced by using electrodes made of metals which do not react with lanthanides (molybdenum and especially tantalum), by using pure mangesium and beryllium oxides for the lining of the crucible, and by conducting the electrolysis in an inert gas atmosphere.

Cerium of a higher degree of purity has been produced on a laboratory scale by the electrolysis of its chloride using a molybdenum cathode, by keeping the metal out of direct contact with the graphite. A diagram of the electrolyzer used is shown in Figure 149.

A graphite crucible serving as the anode is protected against oxidation by placing it inside a nickel crucible, and a molybdenum rod is used as the cathode. To prevent oxidation, the upper part of the rod (i. e., the part outside the melt) is enclosed in a quartz tube. The molten metal is collected in a beryllium oxide crucible placed beneath the cathode on the bottom of the graphite crucible. The cerium produced under these conditions is $\sim$ 99.7% pure. The main contaminants are: Fe 0.02 to 0.04%, Si 0.06 to 0.6%, Mo $<$ 0.01%, Mg 0.01%, Ni 0.4 to 0.6%, Al 0.1 to 0.6%, Be 0.2 to 0.9%, Ca 0.05 to 0.25%.

Electrolyzers of this type have been used for the production of relatively pure metals of the cerium group, as well as the higher-melting metals of the yttrium group. In the case of the yttrium group metals, molten zinc or cadmium (contained in a ceramic crucible on the bottom of the graphite crucible) serves as the cathode. The current is supplied to the liquid cathode by means of a molybdenum rod insulated with a porcelain tube (to prevent contact with the electrolyte). Zinc or cadmium are easily removed from the cathodic alloy by vacuum distillation at 900°.

Metallothermic preparation of the lanthanides /9, 10, 12/

Metallothermic reduction of lanthanide halides (chlorides, fluorides) or oxides produces lanthanide metals of a higher degree of purity than the lanthanides produced by the electrolysis of molten salts.

The data in Table 52 (which contains values of the heats and free energies of formation of lanthanide halides and the common metallic reducing agents) lead to the conclusion that the chlorides may be reduced by calcium or sodium, and the fluorides by calcium. However, when sodium was used to reduce the chlorides, the lanthanide ingots produced could not be easily separated from the slags.

The use of magnesium or aluminum for the reduction of the halides yielded alloys of the lanthanide and the reducing agent, and the yield of the lanthanides (as alloys) was not high enough. Magnesium can be separated from the lanthanides by vacuum distillation above the melting point of the lanthanides; aluminum cannot, however, be quantitatively separated by this method.

The best results as regards yield, quality of the ingot, and purity of the metal were obtained by using calcium to reduce the halides. This method may be used for the manufacture of all the lanthanides except

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samarium, europium, and ytterbium, whose compounds are reduced only to the lower halides. A method was accordingly developed for the production of these three lanthanides by reduction of their oxides with lanthanum and a simultaneous vacuum sublimation of the products.

TABLE 52

Heats and free energies of formation of lanthanide halides, kcal/g-atom of chlorine and fluorine

Element	Chlorides			Fluorides		
	$\Delta H_{298°K}$	$\Delta F_{298°K}$	$\Delta F_{1000°K}$	$\Delta H_{298°K}$	$\Delta F_{298°K}$	$\Delta F_{1000°K}$
La	—88	—82.3	— 69.7	—140.3	—134	—120
Ce	—86.7	—81	— 68.7	—138.7	—132.3	—118.3
Pr	—86	—80.3	— 68.3	—134.3	—131.3	—117.7
Nd	—84.7	—79	— 67	—136.7	—130.3	—116.3
Pm	—84	—78.3	— 66.7	—136	—129.7	—115.7
Sm	—82.7	—77.3	— 65.7	—135	—128.7	—114.7
Eu	—77.7	—72.3	— 61	—130.3	—124.3	—110.3
Gd	—81.7	—76.3	— 65	—134.7	—128.7	—114.7
Tb	—70.3	—65	— 54	—133.3	—127.3	—113.3
Dy	—78.7	—73.3	— 62	—132.7	—126.7	—112.7
Ho	—77.7	—72.3	— 60.3	—131.7	—125.7	—112
Er	—77.3	—72	— 60	—130.7	—124.7	—111
Tu	—76.3	—71	— 58.7	—130.3	—124.3	—111
Yb	—71.3	—66	— 53.7	—125.3	—119.3	—106
Lu	—76	—70.3	—112.7	—130.7	—124.7	—111.3
Na	—98.3	—92	— 76.7	—136	—129	—112.6
Ca	—95.3	—90	— 78.2	—145.1	—139.1	—124.8
Mg	—76.6	—70.5	— 57.6	—131.5	—126	—112.8
Al	—55.6	—51	—	—107.7	—102	— 89.7

Reduction of halides by calcium

The reduction of the halides by calcium must be carried out at temperatures above the melting point of the lanthanides in order to produce a metallic ingot. The slag must also be melted.

It follows that the relatively low-melting metals such as La, Ce, Pr, and Nd (mp in the range 800 to 1050°) must be reduced under conditions differing from those used for the reduction of metals of the yttrium group, whose melting points lie between 1350 and 1650° (see Table 45).

Reduction of chlorides. The low-melting lanthanides (La, Ce, Pr, Nd) may be prepared by the reduction of their chlorides or fluorides with calcium. Metals of a high degree of purity are produced by reducing anhydrous lanthanide chlorides in small hermetically sealed steel containers (bombs) lined with pure magnesium oxide or with a dolomite mixture of calcium and magnesium oxides (Figure 150).

The maximum reduction temperature is 1100°. At that temperature MgO does not react with the lanthanides. However, partial reduction of the MgO (by the molten lanthanides) takes place at higher temperatures and the magnesium is dissolved in the melt. High-purity calcium (purified by vacuum distillation) as grains with a particle size of $\sim$ 0.6 to 1 mm is mixed with the lanthanide chloride in a special chamber in a dry argon atmosphere. The mixing in a dry argon atmosphere is necessary to prevent absorption of moisture by the chloride and of nitrogen by the calcium.

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The calcium is added to the mixture in a ~ 15 to 20% excess over the stoichiometric amount needed for the reaction: $2LnCl_3 + 3Ca = 2Ln + 3CaCl_2$. When the process is carried out on a small scale, the reaction heat does not suffice to melt the produced metal and the slags. To increase the heat of reaction, iodine is added to the charge (0.3 to 0.7 moles iodine/mole chloride) together with an additional amount of calcium needed to form CaI_2*.

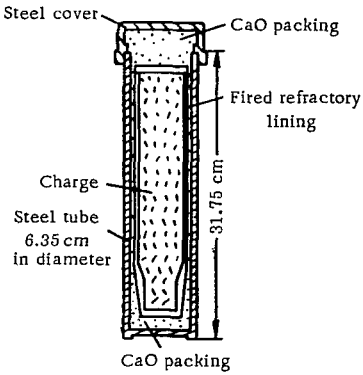

FIGURE 150. Reaction vessel (bomb) used for the thermal reduction of lanthanide chlorides by calcium.

Moreover, the introduction of iodine reduces the melting point of the slag by the formation of a eutectic mixture of $CaCl_2$ and CaI_2. The hermetically sealed vessel containing the charge is heated to 700° in order to initiate the reaction. The metals are produced in an average yield of 95%, in the form of dense ingots which are easily separated from the slag. The metals contain about 2% calcium which is separated by remelting of the metals in vacuo, in magnesium oxide or beryllium oxide crucibles.

Magnesium oxide crucibles cannot be used if the reduction is to be effected at temperatures above 1200° (e. g., in the case of gadolinium). Tantalum is the most suitable reactor material since it does not react with most of the lanthanides below 1500 to 1600°.

The reduction is carried out in a welded tantalum crucible covered with a perforated lid, in an argon atmosphere. High-frequency heating is employed (no heating additives are added to the charge). The lanthanides adhere strongly to the tantalum and the tantalum shell must be removed by mechanical means. In order to save tantalum, the crucibles are made of thin (0.02 to 0.06 mm) foil.

Reduction of the fluorides. Lanthanides with high melting points (Tb, Dy, Ho, Er, Tu, Lu, Y) cannot be produced by the reduction of their chlorides. The main difficulty is the high vapor pressures of the lanthanide chlorides at the temperatures (1500 to 1600°) required for the production of ingots. The boiling points of lanthanide fluorides are higher than those of the chlorides (see Table 46). Moreover, as compared with the chlorides, the fluorides have the advantage of being nonhygroscopic. Thus, their handling is more convenient.

According to American literature, the reduction of the fluorides by calcium is carried out in tantalum crucibles in an argon atmosphere. When mixing calcium with lanthanide fluorides, care is taken to reduce as much as possible the contact with the atmosphere. Calcium is added to the charge in a 10% excess over the stoichiometric amount needed for the reaction:

$$2LnF_3 + 3Ca = 2Ln + 3CaF_2.$$

The charge is packed in a tantalum crucible (which is degassed in advance by heating in vacuo), covered with a perforated lid and placed in

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* The heat of formation of CaI_2 is 128.5 kcal/mole.

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the quartz tube of a vacuum induction furnace. In order to degas the charge the crucible is heated slowly in vacuo to 600°. At that temperature, pure argon is fed into the apparatus until the pressure reaches 500 mm Hg and heating is continued to the temperature at which an active reaction begins between the fluoride and the calcium. Depending on the metal to be produced, that temperature lies between 800 to 1000°. The reaction is exothermic but the heat evolved is not sufficient to reach the required final temperature and the heating must be continued. In order to obtain a high yield of the metal (in the ingot) the temperature at the end of the process must be higher than the melting points of the metal and the slag (the melting point of CaF_2 is 1418°). A temperature of 1450° is sufficient in the case of the low-melting lanthanides and Gd, Tb, and Dy, while temperatures 50° above the melting point are required for lanthanides with higher melting points.

After the temperature of vigorous reaction has been reached, the reaction is completed within a few minutes; the maximum temperature is then maintained for another 15 minutes in order to obtain satisfactory separation of the metal from the slag. Under these conditions, the yield of the metal (in the ingot) reaches 97 to 99%. The mixture is cooled and the brittle slag is easily separated from the metal. The main contaminant in the ingot is calcium (0.1 to 2%). To remove the calcium, the ingot is remelted in vacuo, in the same crucible. Using this method, 300 g of the metal may be produced in a crucible 50 mm in diameter and 200 mm high.

The tantalum concentration in the light lanthanides (from La to Nd) is 0.02 to 0.03%, and in the heavy lanthanides 0.1 to 0.5%. The concentrations of other impurities are: Ca 0.01%, N 0.005%, O 0.03 to 0.1%, C 0.0075%, and F 0.005%.

Reduction of oxides with simultaneous distillation of the metal

We have mentioned that samarium, europium, and ytterbium cannot be produced by the reduction of their chlorides or fluorides with calcium. The compounds are reduced only to the divalent halides. A method for producing these three metals has been developed; the oxides are reduced with lanthanum and the metals formed (which have higher vapor pressures than that of lanthanum, see Table 45) are distilled at the same time:

$$Sm_2O_3 + 2La \rightarrow 2Sm\uparrow + La_2O_3.$$

In one such process, the reduction is carried out in a tall tantalum crucible with an air-cooled copper condenser fitted in its upper part*. A mixture of the oxide and lanthanum turnings (taken in a ~ 20% excess) is placed in the tantalum crucible and its lower part is heated to 1400° in a vacuum induction furnace. A vacuum of at least 10^{-4} mm Hg is maintained during the heating. The beginning of the sublimation is accompanied by a sharp drop in the pressure (to about 10^{-7} mm Hg) since the evaporating

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* To prevent contamination with copper, the surface of the condenser is coated with a thin layer of the oxide of the metal to be produced.
A suspension of the oxide in alcohol is used for the coating.

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metals actively absorb the residual gases. The metals are condensed at 300 to 400° when they are obtained in the form of a coarsely crystalline crust. Metallic powders are obtained at lower temperatures.

Samarium, europium, and ytterbium, produced by the above process, are virtually free of tantalum and lanthanum. The concentrations of C, N, O, and H do not exceed 0.01%.

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Part Three

THE SCATTERED METALS

Chapter VII

GERMANIUM

77. GENERAL DATA ON GERMANIUM

On the strength of his periodic system, Mendeleev made in 1870 a very accurate prediction of the properties of a hitherto unknown Group IV element – "eka-silicon". In 1886, i. e., 15 years later, Winkler discovered a new element, germanium, in the mineral argyrodite $4Ag_2S \cdot GeS_2$. The properties of germanium coincided with the properties of "eka-silicon" as predicted by Mendeleev.

Germanium became of practical interest only during the Second World War as a result of the development of semiconductor electronics. The commercial production of germanium for that branch of technology began in 1945 — 1950.

Properties of germanium

Germanium is a light-gray element, with a diamond-type cubic lattice and a lattice parameter $a = 5.657$ Å (Figure 151). Each germanium atom is surrounded by four equidistant atoms positioned on the vertexes of a tetrahedron; the atoms are bonded through paired valency electrons.

Some **physical properties** of germanium are listed below:

Atomic number	32
Atomic weight	72.6
Density, g/cm^3:	
solid (25°)	5.323
liquid (1000°)	5.557
Decrease in volume on melting, %	5.5
Melting point, °C	958.5
Boiling point, °C	2690
Heat of fusion, kcal/g-atom	8.3
Heat of vaporization, kcal/g-atom	84.0
Heat capacity, cal/g °C at 0 — 300°C	0.0768
" " " " 900°C	0.085
Heat conductivity at 25°C, cal/cm·sec·°C	-0.14
Linear expansion coefficient at:	
0 — 300°C	$6.1 \cdot 10^{-6}$
300 — 650°C	$6.6 \cdot 10^{-6}$
Mohs hardness	6 — 6.5
Compressibility coefficient (up to 0 — 12,000 kg/mm^2), cm^2/kg	$1.4 \cdot 10^{-6}$
Surface tension, dynes/cm	600
Electrode potential (s. h. e.), V	-0.15
Magnetic susceptibility, CGS units	$-0.12 \cdot 10^{-6}$
Thermal neutron capture cross section, barns	2.8

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Even very pure germanium is brittle at room temperature, but it becomes ductile at temperatures above 550°.

Like silicon, germanium is a semiconducting material and thus finds increasing use in semiconductor electronics. In this connection, we shall briefly review the most important properties of semiconductors.

The concept of semiconductors. The electrical properties of germanium /1 to 4, 12/. From the standpoint of their electrical conductivity, substances are classified into three groups. Substances with a high electrical conductivity (γ), in the range 10^4 to 10^5 $ohm^{-1} \cdot cm^{-1}$ (i.e., metals and alloys) are known as conductors. Insulators are substances which conduct virtually no current (e.g., quartz, mica, asbestos, etc.) and whose γ is in the range 10^{-14} to 10^{-15} $ohm^{-1} \cdot cm^{-1}$. Substances with an intermediate conductivity ($\gamma = 10^2$ to 10^{-10} $ohm^{-1} \cdot cm^{-1}$) are known as semiconductors; this groups comprises a number of elements (silicon, germanium, selenium, tellurium, etc.) and various compounds (some oxides, sulfides, intermetallic compounds, etc.).

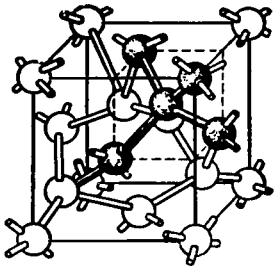

FIGURE 151. The crystalline structure of germanium. Each atom is bound to four adjacent atoms on the points of a tetrahedron.

The differences in the conductivity of these three groups of substances can be satisfactorily explained by means of the so-called zone* theory which is summarized below.

It is known that the electrons in atoms occupy certain discrete energy levels (quantum levels). The transition of an electron from one level to another is accompanied by a change in its potential energy. The electrons in the outer shell are known as valency electrons. Since a solid substance behaves as a single electronic system, the energy levels (zones) of the whole solid may be considered instead of the energy levels of the individual atoms, even though the magnitude of the energy levels of the solid differs from that of the individual atom. Each body has a zone which is completely or partially filled with electrons (known as the filled or valency zone) and a conductivity (or excitation) zone. These two zones are separated by the forbidden zone whose width determines the conductivity of the substance**.

As is evident from Figure 152, conductors, semiconductors, and insulators differ in the width of their forbidden zones. In conductors the forbidden zone is practically nonexistent, i.e., all the electrons in the valency zone readily pass (with a very small loss of energy) into the conductivity zone. In insulators the forbidden zone is wide. The transfer of electrons from the valency zone to the conductivity zone requires the expenditure of such large amounts of energy that these substances have virtually no electrical conductivity. In semiconductors, the forbidden zone is narrow. The transfer of electrons into the conductivity zone requires a relatively small amount of energy (heating, illumination, or the application of a potential difference).

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* [or "band" theory.]

** It must be noted that the location of an electron at a certain energy level designates its potential energy rather than its geometrical (physical) position.

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Two types of conductivity may be distinguished in semiconductors — electron and hole type conductivity*. Both types of conductivity are the result of the disturbance (caused by heat, illumination, etc.) of the separate valency bonds between the paired electrons and the transfer of electrons into the conductivity zone (Figure 153). When an electrical field is acting on the body, the free electrons move in a certain direction creating an electrical current. Such conductivity is known as n-type conductivity.

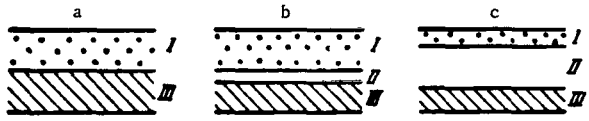

FIGURE 152. Energy zones.

a—conductors; b—semiconductors; c—insulators; I—conductivity zone; II—forbidden zone; III—valency (filled) zone.

However, another type of conductivity may also exist. An empty space (known as a hole) remains when some external force causes the removal of an electron from the valency zone; this hole may be regarded as a positive charge of a magnitude equal to that of the electron charge. It is possible to have electron transfers (caused, for instance, by thermal fluctuations) from the filled lattice points to the adjacent unfilled points (holes). Such transfers create new holes. The electric field produces a directed motion of the holes which is equivalent to the motion of positive charges. Such conductivity is of the hole type (p-type).

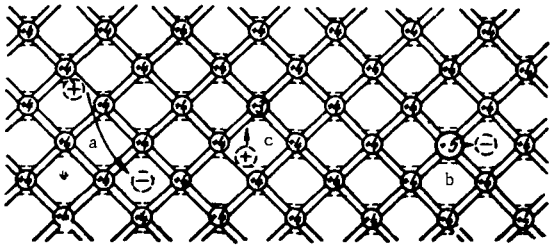

FIGURE 153. The mechanism of n-type and p-type conductivity in germanium (each double line represents bonds between germanium atoms consisting of paired electrons).

a—rupture of an electron bond caused by the transition of an electron into the conductivity zone and the formation of a hole; b—donor atom in the lattice (e.g., As^{5+}) in which the fifth electron is weakly bound and passes into the conductivity zone; c—acceptor atom in the lattice (e.g., In^{3+}) to which the missing electron is supplied at the expense of the adjacent electron bond, in which a hole is left.

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* [Or "n-type" and "p-type" conductivity, respectively.]

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In the ideal case (i. e., semiconductor crystals not containing impurities) the number of free electrons equals the number of holes, and the contributions of electrons and positive charges (holes) to the conductivity are equal. Such conductivity is known as inherent conductivity. The addition of small amounts of other elements may create conditions such that the numbers of electrons and holes are not equal. In such a case (depending on the nature of the additive) the conductivity is created preferentially through the motion of either electrons (n-type semiconductors) or holes (p-type semiconductors).

Some of the additives which create an n-type conductivity in germanium (the so-called donor additives) are elements whose valency is higher than four, e. g. , arsenic, antimony, and phosphorus. This is because when a pentavalent element replaces a germanium atom in the lattice, the fifth electron is weakly bound to the atom and readily passes into the conductivity zone (see Figure 153). The additives producing p-type conductivity (acceptor additives) comprise elements with a valency below four — indium, gallium, aluminum, copper, zinc, etc. One unfilled lattice point remains when the atom of a trivalent element replaces an atom of tetravalent germanium. In such a case the number of holes is greater than the number of electrons.

The conductivity of semiconductors is strongly affected by external factors such as illumination, heat, and electric field. The effect of a light beam on the conductivity is known as the photoelectric effect.

One of the important properties of semiconductors is that a thin film which conducts the current only in one direction is created on the boundary when semiconductors of different types (n- and p-type) are brought into contact. This film is known as the barrier layer. Accordingly, semiconductors may be used as rectifiers.

Some of the electrical properties of germanium, which are of value for its characterization as a semiconductor, are listed below:

Width of forbidden zone, ΔE, eV	0.7
Electron mobility*, μ cm^2/V·sec	3900
Hole mobility*, μ cm^2/V·sec	1900
Specific resistance of high-purity germanium monocrystals (at 25° C), ohm·cm.	55—60

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* The mobility of the current carriers (μ) is a measure of the drift (motion) rate of electrons or holes in an electric field with an applied voltage of one volt.

The above value of the specific resistance is that of very pure germanium, and is close to the inherent resistance of germanium. The specific resistance of germanium is sharply reduced by the presence of impurities. As with all semiconductors, the specific resistance of germanium decreases with increasing temperature. There is a characteristic dependence of the electrical resistance of germanium on the pressure.

Chemical properties of germanium. Pure solid germanium is not attacked by air at ambient temperature, but is rapidly oxidized at 600 to 700° with the formation of germanium dioxide.

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The action of ammonia on germanium or germanium dioxide at 700 to 800° results in the formation of germanium nitride Ge_3N_2. The nitride is not decomposed by water, dilute alkalies, or acids. It dissociates at about 1000°.

A vigorous reaction between germanium and chlorine is observed at room temperature, with the formation of $GeCl_4$ (bp 83°). Germanium reacts with bromine and iodine on heating. Sulfur vapor reacts with germanium, yielding GeS.

Germanium is not attacked by hydrochloric or dilute sulfuric acids. The metal is slowly dissolved by hot concentrated sulfuric acid, with the evolution of SO_2. Nitric acid reacts with germanium, yielding the hydrated dioxide $GeO_2 \cdot nH_2O$. The metal is readily dissolved by aqua regia. Alkali solutions have little effect on germanium, but it is rapidly dissolved by molten alkalies in the presence of air.

Germanium dissolves in dilute hydrogen peroxide solutions, yielding pergermanic acid.

Germanium forms no carbides. It can be fused in a graphite crucible without significant contamination with carbon.

The properties of germanium compounds

Compounds of tetravalent and divalent germanium are known; the former are more stable. Some of the technologically important germanium compounds are described below.

Germanium oxides and hydroxides. Germanium dioxide (a white powder) is the main starting material for the production of metallic germanium. It is produced by the dehydration of the hydrate ($GeO_2 \cdot nH_2O$) precipitated during the neutralization of solutions containing germanium salts (chloride, sulfate, nitrate).

The melting point of GeO_2 is 1115°. Appreciable vaporization of the dioxide occurs above 1250°. The heat of formation of GeO_2 is 128 kcal/mole. The dioxide is reduced to the metal by hydrogen above 600°.

In contrast to silicon dioxide, germanium dioxide is appreciably soluble in water. The solubility at 20 and 100° is 0.4 and $\sim$ 0.95% respectively. Germanium dioxide dissolves in alkalies with the formation of germanates. Alkali germanates are soluble in water; the germanates of the alkaline-earth and heavy metals are sparingly soluble in water but are readily decomposed by acids.

Germanium monoxide GeO (a dark-gray powder) is formed when germanium dioxide is reduced by hydrogen or carbon monoxide. Appreciable sublimation of GeO occurs above 700°. The hydroxide $Ge(OH)_2$, corresponding to germanium monoxide, is precipitated as an orange-yellow precipitate on the addition of alkali hydroxides to solutions containing Ge^{2+} ions. The hydroxide $Ge(OH)_2$ is amphoteric. When dissolved in alkalies the hydroxide yields germanates (e.g., $NaHGeO_2$).

Germanium sulfides. Germanium forms two sulfides: GeS_2 (white) and GeS (brown).

Germanium disulfide is precipitated by hydrogen sulfide from acid solutions. The acid must have a concentration of 4 to 5 N. GeS_2 undergoes hydrolysis in solutions of lower acidity:

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$$GeS_2 + (n+2)H_2O \rightleftarrows GeO_2 \cdot nH_2O + 2H_2S.$$

Partial dissociation of GeS_2 (to GeS and sulfur) occurs in inert media at temperatures above 400. The "apparent vapor pressure" of GeS_2 at 550° is $2.5 \cdot 10^{-3}$ mm Hg. Above 400° the disulfide is oxidized in air. The disulfide dissolves in alkali sulfides or alkali solutions with the formation of sulfogermanates. The dissolution of the disulfide in ammonium sulfide yields a sulfide with the formula $(NH_4)_6Ge_2S_7$.

Germanium monosulfide GeS is produced as a result of the reduction of GeS_2 by hydrogen or its thermal dissociation. It is characterized by its appreciable volatility at temperatures above 450°.

The vapor pressure of GeS at various temperatures is given below:

Temperature, °C	400	450	500	550	600
Vapor pressure, mm Hg	0.25	1.60	3.48	14.21	40.96

Germanium monosulfide is soluble in hydrochloric acid and alkali solutions.

Germanium halides. Germanium forms volatile halides of the type GeX_4, where X is F, Cl, Br or I. Germanium tetrachloride $GeCl_4$ is of importance in technology. The chloride is produced by dissolving germanium dioxide in 6 N HCl or by chlorination of germanium compounds (with chlorine). Germanium tetrachloride hydrolyzes in acids with a concentration below 6 N, with the precipitation of the hydrated germanium dioxide.

$GeCl_4$ is a colorless liquid with a boiling point of 83°. The chloride distils over when a hydrochloric acid solution containing germanium tetrachloride is boiled. The solubility of $GeCl_4$ in hydrochloric acid is strongly affected by the acid concentration. Thus, the solubility of $GeCl_4$ in 16 and 7.77 N HCl is 0.88 and 85.36 g $GeCl_4$/1000 g solution respectively.

Germanium hydrides (germanes). Germanium forms hydrogen compounds which resemble the hydrogen compounds of silicon (silanes) and of carbon (hydrocarbons).

Monogermane GeH_4 is a colorless gas at ambient temperatures. It condenses at -83°. Monogermane may be prepared by the decomposition of magnesium germanide with hydrochloric acid:

$$GeMg_2 + 4HCl = GeH_4 + 2MgCl_2.$$

At temperatures above 280° GeH_4 is dissociated into germanium and hydrogen. The homologues of GeH_4 — Ge_2H_6 and Ge_3H_8 — are colorless liquids. In germanes hydrogen may be replaced by halogen atoms. Such a substituted compound is germanochloroform $GeHCl_3$ — a liquid with a boiling point of 75°.

Uses of germanium /5/

As a semiconductor, germanium is of importance in electronics. It is used for the production of crystal rectifiers (diodes) and amplifiers (triodes). Crystal rectifiers and amplifiers have several advantages over vacuum tubes: they require considerably less power and they have a longer service life; as compared with vacuum tubes, semiconductor devices

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are more stable to mechanical vibration and impact, and are much smaller in size. Since no energy is used to heat the emitter (as in vacuum tubes), the efficiency of crystal amplifiers attains 40 to 50%. All these advantages favor the use of crystal rectifiers and amplifiers, especially so in complex computers, remote control, and radar setups.

Rectifying contacts (known as p-n or n-p junctions) are produced in germanium monocrystals through the diffusion of impurities to the surface layer of a germanium plate. One commonly used method for the formation of a rectifying contact is the application of molten indium to the surface of a plate of n-type germanium. As a result of the diffusion of indium atoms into the germanium, a thin layer with p-type conductivity is created at the contact site.

In addition to its use as rectifiers in radio receivers, germanium has been recently used as high-power rectifiers of standard frequency AC, for currents of 6000 to 10,000 amp or more. These rectifiers are characterized by their high efficiency (the direct current produced is 95% of the alternating current used). Germanium rectifiers operate at current densities which exceed several times the maximum permissible current density in selenium and other rectifiers. They are small in size and are especially convenient to move from place to place.

Germanium triodes are extensively used for the amplification, generation, or transformation of electrical oscillations. There are two types of triodes: $n-p-n$ and $p-n-p$. In $n-p-n$ triodes two layers of n-type germanium are separated by a thin layer with a p-type conductivity, while in $p-n-p$ triodes the center layer has n-type conductivity while the external layers are of p-type (see Figure 154).

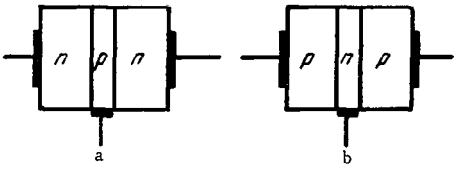

FIGURE 154. Diagram of a germanium triode.

a - $n-p-n$ triode; b - $p-n-p$ triode.

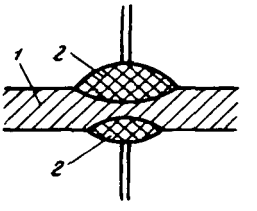

FIGURE 155. Diagram of a semiconductor triode with junction-type contacts.

1 — germanium; 2 — indium.

A diagram of a triode of the $p-n-p$ type, in which p-type conductivity is created in the external layers by fusing drops of indium onto a plate of n-type germanium, is shown in Figure 155. Such triodes are small and weigh only a little over 1 gram.

Like other semiconductors, germanium is used for the production of thermistors. These devices make use of the fact that the electrical resistance of germanium is strongly affected by the temperature, which makes it possible to determine the temperature from the variation in the electrical resistance. Small germanium plates, serving as thermistors, may be used to measure the temperature anywhere in a room, in pipes,

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vessels, and various mechanisms, so that automatic signalization and control are readily effected. Thermistors are also used in time relays and in instruments ensuring a gradual (at any desired rate) increase of the current in a circuit.

Germanium is used for the production of photocells with a barrier layer and of thermoelements.

Germanium film resistors are used in radio technology. A thin film deposited on glass by thermal dissociation of the gaseous monogermane GeH_4 or germanium halide ($GeCl_4$, GeI_4) has a resistance between 1000 ohms and several megohms.

Other uses of germanium are of secondary importance. Thus, for instance, uses have been proposed for some germanium alloys. An aluminum-germanium alloy (74% Al, 21% Ge, 2% Fe, and 3% Si) has been recommended for the production of vacuum tube cathodes. The use of the low-melting eutectic Au—Ge alloy (12% Ge, mp 356°) has been proposed to obtain hard coatings on gold and for improving the quality of the gold solders. The presence of small amounts of germanium improves the fatigue and corrosion resistance of magnesium castings and increases their creep strength.

The production of germanium in the Western countries in 1960 to 1962 is estimated at 60 to 70 tons. The production volume at the present time is very probably higher.

78. OCCURRENCE

The concentration of germanium in the Earth's crust is $7 \cdot 10^{-4}$ % by weight. Most of the germanium is scattered in silicates, sulfides, and complex sulfide minerals. The concentration of germanium in zinc, copper, lead, and iron sulfides ranges from a few thousandths to a few tenths of one percent. The highest concentrations of germanium (0.01 to 0.1%) are encountered in low-temperature zinc blendes. There are several minerals (of the thio salt type) with high germanium contents. Some of these are listed below.

Argyrodite Ag_8GeS_6 contains 5 to 7% Ge (the element germanium was discovered in argyrodite).

Germanite $Cu_3(Fe, Ge, Ga, Zn)(As, S)_4$ (this formula is only approximate) contains 6 to 10% Ge, 6 to 8% Fe, and 0.5 to 0.8% Ga. This mineral was found for the first time in 1918 in the copper-lead-zinc ores of Tsumeb in South-West Africa.

Renierite $(Cu, Fe)_3(Fe, Ge, Zn, Sn)(S, As)_4$ contains 6.37 to 7.8% Ge. The mineral was found in the copper-zinc ores of Katanga.

In addition to sulfide ores, various coals also serve as a source of germanium. The germanium content of coals of various types fluctuates between 0.001 and 0.01%, and the germanium is preferentially concentrated in coals of a low degree of metamorphization (anthracite coals contain almost no germanium). It has been found that the lower the ash content of the coal, the higher its germanium content /13/.

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Behavior of germanium during processing of sulfide raw materials

During the beneficiation of sulfide ores containing several metals, the germanium is concentrated in the zinc, copper, or mixed zinc-copper concentrates, depending on the form in which it occurs in the raw material (the germanium may be present either as an isomorphous impurity in the sulfides or as minerals of the germanite or renierite types).

The production of zinc. In the pyrometallurgical (distillation) process for the production of zinc, zinc concentrates are subjected first to an oxidative and then to an agglomerative roasting in sintering equipment. Because of the high temperature during the agglomerative roasting (1200 to 1300°) a fraction of the arsenic, lead and cadmium in the material to be roasted is vaporized. In the process a considerable fraction of the germanium (as chloride or oxides) is expelled with the gases and concentrates in the dust entrapped in the electrostatic filters or some other dust trap.

During the distillation of the zinc in retort furnaces germanium (which has a high boiling point) accumulates in the retort residues in which its concentration may occasionally reach a few hundredths or a few tenths of one percent.

In the hydrometallurgical production of zinc most of the germanium is concentrated in the solid wastes from the leaching of zinc cinders. The concentration of germanium in the zinc sulfate solutions taken for electrolysis must not exceed 0.1 mg/l since the presence of germanium interferes with the electrolytic deposition of the zinc (prevents the formation of a continuous layer of zinc and causes dissolution of the zinc cathode).

During the processing of zinc cakes (leaching residues) by the sublimation method (the so-called rotary-kiln process), germanium is concentrated in the distillate (oxides). This is attributed to the volatility of germanium monoxide GeO.

Thus, germanium may be produced as a by-product of zinc manufacture from the following materials: dust from agglomerative roasting, retort residues, solid residues from the leaching of zinc cinders, and from oxides of the rotary-kiln process.

The production of copper /10/. During the roasting of germanium-containing copper and copper-zinc concentrates, most of the germanium remains in the cinders since the germanium dioxide formed is nonvolatile under the roasting conditions (800 to 850°). A fraction of the germanium may be lost through the interaction of GeO_2 with sulfides and the formation of GeS, which is volatilized at these temperatures:

$$3GeO_2 + 4Fe(Zn)S \rightarrow 3GeS + 4Fe(Zn)O + SO_2.$$

In most cases the roasted or crude concentrates are taken for the smelting of matte in reverberatory furnaces. In addition, the matte is smelted directly from copper ores in shaft furnaces (the so-called "water-jackets").

The distribution of germanium between the products of the reverberatory smelting of copper concentrates depends on the concentration of sulfur (in the form of sulfides) in the starting raw material. In the smelting of

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of the crude concentrates, most of the germanium (80 to 90%) passes into the matte, and the remaining germanium is distributed between the slags and the dust. In the smelting of roasted concentrates most of the germanium (60 to 80%, depending on the degree of roasting) passes into the primary slags, while the remaining 20 to 40% is distributed between the matte and the dust. The highest germanium content is usually observed in the dusts.

TABLE 53

Approximate composition of the dust formed in the smelting of copper concentrates in water-jacketed furnaces

Element	Copper concentrates from Katanga (Africa) %	Copper concentrates from Mansfeld (East Germany) %
Ge	0.36	0.007—0.008
Zn	28	23.6—31.36
Pb	25	16.35—19.5
Cd	3	0.10—0.13
Cu	1.5	0.66—1.06
As	7.3	Not determined
Cl	Not determined	0.6—1.19
Sulfur	" "	15.1—19.9
Bitumen	" "	6.34—7.10

In the shaft smelting of copper concentrates, the degree of volatilization of the germanium is higher than in reverberatory smelting. The distribution of germanium after semipyritic smelting in one Soviet plant was as follows: in the dust 40%, in the matte 18%, and in the slags 42%. When using a charge with a germanium content of 3 g/ton, the germanium concentration in the coarse and fine dusts was 20 and 60 g/ton respectively.

The main components of the dust are zinc, lead, cadmium, and arsenic. The concentration of germanium in the dusts from shaft smelting varies from a few thousandths to a few tenths of one percent (Table 53).

The distribution of germanium between the products of the processing of copper matte by the Bessemer process (in converters) is as follows: in the slags 80 to 90%, in the dust 11 to 16%, and in the crude copper 2 to 5%. When the germanium content of the matte is 0.0003 to 0.0005%, the germanium concentration in the dust from the converters is 0.0015 to 0.0035% (the germanium is probably volatilized as GeS, and to a certain extent as GeO).

The passage of most of the germanium into the slag is attributed to the interaction of germanium dioxide with basic oxides, yielding germanates of the Me_2GeO_4 type. When slags from the copper smelting industry are processed by blowing a mixture of air and coal dust through the fused slags (the so-called "fuming process), most of the germanium is volatilized as GeO and is collected together with the zinc oxide and other oxides.

Thus, the following materials from copper manufacturing may serve as sources of germanium: dust from shaft and reverberatory smelting, converter dust, and the volatilized product from the processing of slags

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by the fuming process. It must be noted that the largest fraction of the germanium (of its total content in the raw material) passes into the slags, although its concentration in the dusts is higher than in the slags.

Behavior of germanium in the processing of coals

In the complete combustion of coals (e.g., in the combustion chambers of boilers), most of the germanium remains in slags and in the ash. Thus, the distribution of germanium in the residue from complete combustion (in an excess of air) of brown coal containing 0.009% Ge was (in%):

In slags	51.7	70.7
In ash	19.0	
In dust	0.25	
Losses through entrainment with gases	29.0	

When the same coal was burned in a deficient supply of oxygen (e.g., in gas generators), the distribution of germanium was different. About 75% of the germanium passed into the dust from the flues and 25% of the germanium passed into the ash and slags. This is attributed to the fact that the volatile germanium monoxide GeO is formed in reducing medium. The concentration of germanium in the dust and carbon black from gas-producing plants sometimes attains 1%. Thus, the germanium concentration in the dust from gas-producing plants in England is 0.29 to 1.24%. The dust also contains 0.38 to 0.75% Ga_2O_3.

In coke-chemical plants, germanium occurs at higher concentrations in the ammoniacal (tar-supernatant) waters and the tar products, which may be used as sources of germanium /13/.

79. EXTRACTION OF GERMANIUM FROM VARIOUS RAW MATERIALS

The composition of the starting raw material determines the selection of the process to be used for the primary processing carried out to prepare products enriched in germanium and to separate out some of the elements present in the material. The germanium-enriched product is usually processed to yield technical grade germanium tetrachloride, which is afterwards purified.

Primary processing of germanium-containing products

Leaching the material with sulfuric acid, and subsequent isolation of germanium from solution. In the case of sulfide-containing materials, an oxidative roasting is carried out prior to the leaching. Most of the lead is separated from germanium after the sulfuric acid leaching. Germanium is precipitated from the sulfuric acid solution by cementation on zinc dust.

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By adding a controlled amount of the dust, germanium may be precipitated together with copper and arsenic, leaving the less noble cadmium and other elements in solution. In some processes germanium is precipitated from the acid solutions by hydrogen sulfide as germanium disulfide GeS_2.

Sublimation of germanium sulfide GeS or monoxide GeO in a reducing medium. This method of concentration of germanium may be used for the extraction of germanium from ore concentrates, dusts, coal, and other types of raw materials. Either sulfur or pyrite may be used as the sulfurizing agents.

Sulfatizing roasting of the material. In order to convert germanium and other components of the raw material into their respective sulfates, the material is heated with sulfuric acid to 450 to 500° and the product is leached with dilute sulfuric acid. During the sulfatizing roasting, most of the arsenic is evolved with the gases as As_2O_3. The germanium is isolated from the solution.

Fusion of the material with sodium hydroxide. The fusion of the material with sodium hydroxide yields soluble sodium germanate which is leached with water together with other soluble salts (sodium silicate, aluminate, and arsenate). The hydrated germanium dioxide is then precipitated from the solution in a certain pH range.

The reductive smelting of the material in the presence of copper or iron is based on the concentration of the germanium in the copper or iron alloy, from which it is then extracted by treating with hydrochloric acid.

Production of technical grade germanium tetrachloride from the concentrates

The products, enriched by one of the above processes and containing 2 to 10% germanium, are usually processed with hydrochloric acid.

The material is treated with concentrated hydrochloric acid at temperatures up to the boiling point of the acid. As a result $GeCl_4$ is distilled together with a fraction of the hydrochloric acid and is condensed. Germanium can be separated from most other elements (Fe, Cu, Cd, Zn, Pb, Si, etc.) in this way.

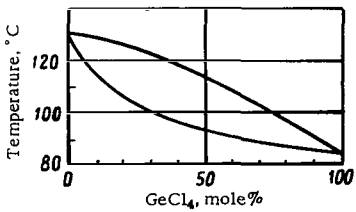

FIGURE 156. Phase diagram of the system $GeCl_4 - AsCl_3$.

Arsenic chloride is volatilized together with $GeCl_4$. The boiling point of $AsCl_3$ is 130°. However, it has an appreciable vapor pressure at the boiling point of $GeCl_4$ (83°). This, and the fact that $AsCl_3$ and $GeCl_4$ form a continuous series of liquid solutions (Figure 156), explain the fact that the $AsCl_3$ distils over together with the germanium chloride. In order to separate the bulk of the arsenic, the As^{3+} is oxidized to As^{5+} with the aid of chlorine. This leads to the formation of arsenic acid which remains in the solution:

$$AsCl_3 + Cl_2 + 4H_2O \rightarrow H_3AsO_4 + 5HCl.$$

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The condensed technical grade germanium chloride is then purified by one of the methods described below (Section 81).

The material is treated with HCl in distillation vats, consisting of enameled steel boilers with steam jackets and bottom discharge. The boilers are fitted with stirrers and lids, through which pass tubes for the introduction of chlorine and the removal of the $GeCl_4$ vapors into the condensers. The germanium-containing material and hydrochloric acid are charged into the boilers and chlorine is bubbled through the solution (in order to oxidize the arsenic) to saturation, or else pyrolusite MnO_2 (which reacts with the HCl, with evolution of Cl_2) is added to the solution. The pulp is then heated and $GeCl_4$ is distilled by passing a slow stream of chlorine. The $GeCl_4$ vapors are fed to a refractory-glass condenser cooled with brine to -10°.

80. EXAMPLES OF PROCESSES FOR THE EXTRACTION OF GERMANIUM FROM RAW MATERIALS

Extraction of germanium from the dusts formed in the agglomeration roasting of zinc concentrates /14, 17/

A flow sheet of the extraction process of germanium from zinc concentrates containing 0.01 to 0.015% Ge, employed at one plant in the USA, is shown in Figure 157.

The cinders from the oxidative roasting of the concentrate are mixed with coal and fluxes and are subjected to agglomeration roasting at 1200 to 1300°. Germanium (together with cadmium and lead) concentrates in the dusts which are trapped in electrostatic filters. The dust is leached with sulfuric acid; the leach liquor contains the copper, cadmium, zinc, arsenic, and germanium from the dust. Lead is separated as sulfate. A calculated amount of zinc dust is added to the solution when copper, germanium, and arsenic are separated by cementation on the zinc. The bulk of the cadmium remains in solution, from which it is then extracted. A germanium concentrate, containing 4 to 7% germanium, is produced by dissolving the cemented precipitate and a second cementation on zinc.

The germanium concentrate is dried, subjected to oxidative roasting, and treated with concentrated hydrochloric acid heated to the boiling point. Germanium tetrachloride is distilled and trapped in ice-cooled condensers together with the arsenic chloride (present as an impurity) and the hydrochloric acid.

Because of the low solubility of $GeCl_4$ in concentrated hydrochloric acid, the condensate in the condenser separates into two layers: the lower layer consists of $GeCl_4$ and the upper of HCl. Arsenic chloride is distributed between the two layers. The technical grade germanium chloride obtained is forwarded to purification.

Extraction of germanium from the copper concentrates of Tsumeb /16/

The copper-zinc-lead ores from Tsumeb (South-West Africa) contain germanium as the minerals germanite and renierite.

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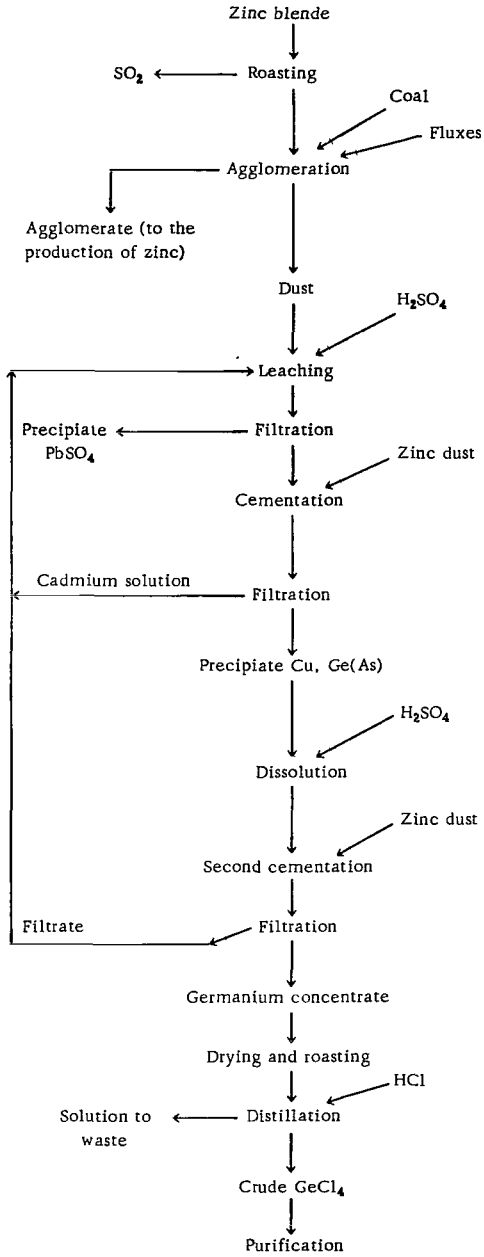

FIGURE 157. Flow sheet of the extraction of germanium from the dust formed in the agglomeration roasting of zinc concentrates.

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Beneficiation of these ores (by flotation) yields copper concentrates containing 0.2 to 0.4% Ge. The average composition of the concentrates is: 0.25% Ge, 25.0% Pb, 27.8% Cu, 7.92% Zn, 7.5% As, 22.2% S, and 2.3% Fe.

Germanium is extracted by a method based on the sublimation of germanium monosulfide, as a result of the heating of the concentrate in a neutral or a reducing atmosphere. In a H_2 or CO atmosphere, 90 to 93% of the germanium is sublimed at 800°. In a neutral atmosphere (e.g., in flue gas, containing mainly N_2 and CO_2) the same extent of sublimation is obtained only at 1000°. In a CO atmosphere, the volatilization of lead at 800 to 900° is insignificant. The arsenic is sublimed, together with the germanium. In a CO atmosphere arsenic sulfide is reduced as follows:

$$As_2S_3 + 3CO \rightarrow 2As + 3COS.$$

The metallic arsenic is readily volatilized and condensed. Carbonyl sulfide COS is ignited at the point of issue of the gases from the condenser, yielding CO_2 and SO_2. The GeS sublimate is subjected to oxidative roasting, with the simultaneous volatilization of the arsenic in the form of As_2O_3. The oxide residue is enriched in germanium. It is treated with hydrochloric acid and the $GeCl_4$ is distilled. The distribution of the germanium, the composition of the products, and their yield in each operation are shown in Table 54.

TABLE 54

Distribution of germanium between the products of processing of germanium concentrates (from Tsumeb) by the sulfide sublimation method

Product	Yield, %	Concentration, %			Distribution, %		
		Ge	As	Pb	Ge	As	Pb
Germanium concentrate	100	0.25	7.5	26.0	100.0	100.0	100.0
Nonvolatilized fraction (sulfides residue)	85.0	0.024	0.15	28.8	8.3	1.7	94.2
Oxide enriched in germanium	2.7	8.5	3.2	55.5	91.5	1.1	5.7
Arsenic oxide sublimate	0.7	0.005	75	0.15	0.2	97.2	0.1

The flow sheet of the process is shown in Figure 158. The sublimation is carried out in vertical retort furnaces. The retort is made of carbofrax* and is externally heated with the flue gases. The pelletized charge is introduced into the retort through a special hermetically sealed device. Before pelletizing, the powdered concentrate is mixed with 10% of petroleum pitch, in order to prevent softening of the pellets (due to the formation of low-melting eutectic mixtures of copper and lead sulfides). The addition of the petroleum pitch separates the sulfide particles. Coal, coke or peat powders, or even sawdust may be used instead of the pitch. In order to prevent sintering of the pellets, the pellets (dried in advance to a moisture content of 2%) are mixed with crushed charcoal or coke before being fed into the furnace.

The maximum temperature in the retort is 870 to 980°. Producer gas (28 to 30% CO, 2% H_2, remainder nitrogen) is introduced into the bottom

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* A refractory material based on carborundum (silicon carbide).

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and top of the retort. The effluent gases, at 700°, are withdrawn at the maximum temperature point (i. e., from the center of the furnace shaft) in order to prevent premature condensation of the sulfide and arsenic vapors. The sublimates, consisting of germanium sulfide, arsenic, lead, and a small fraction of zinc, are trapped in water-cooled condensers, dust chambers, and bag filters. About 80% of the germanium is trapped in the condensers, and 20% in the bag filters. Since the arsenic-containing dust is explosive, provision must be made for protective devices (explosion valves) against air leaks into the system during discharge. The collected sublimates are subjected to oxidative roasting in the form of a thin layer on trays, in an electrical muffle furnace at 550°. Arsenic oxide is trapped in bag filters and the residual oxide mixture is used for the extraction of germanium by distillation.

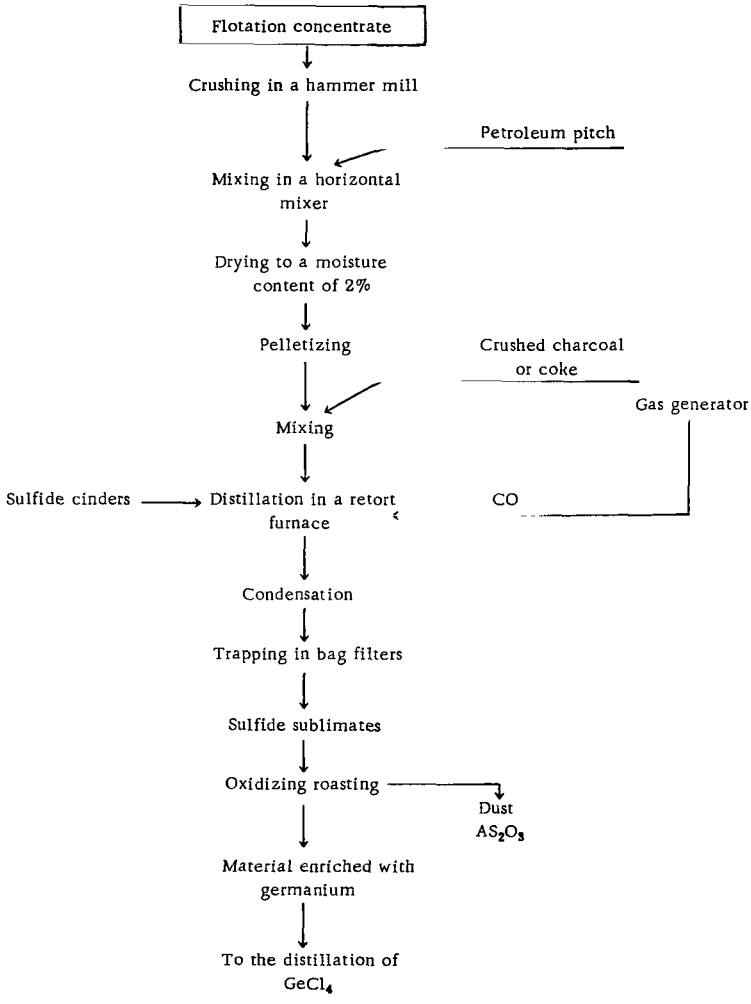

FIGURE 158. Flow sheet of the extraction of germanium from the Tsumeb concentrates by the sulfide sublimation method.

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Extraction of germanium from the dusts formed in the shaft smelting of copper concentrates from Katanga /16/

The dust serving as raw material contains 0.36% Ge, 28% Zn, 3% Cd, 25% Pb, 1.5% Cu, and 7.3% As. The flow sheet for the processing of this dust is shown in Figure 159. The processing comprises the following main operations: sulfatizing roasting, leaching of the sulfatized dust with sulfuric acid, oxidation of the arsenic and its subsequent precipitation, and the isolation of a product enriched in germanium.

The dust discharged from the bag filters is moistened to a moisture content of 20% and is stored in pits. The caked material is crushed in a percussive-disc mill (disintegrator) and is mixed with water and sulfuric acid in a screw-type mixer. The paste-like mass is fed into a rotary kiln (1 m in diameter and 22 m long). It is fired for 4 hours at 450 to 500°. The productivity of the furnace is 700 to 820 kg of dry dust per hour. About 90% of the arsenic is removed with the gases during the firing.

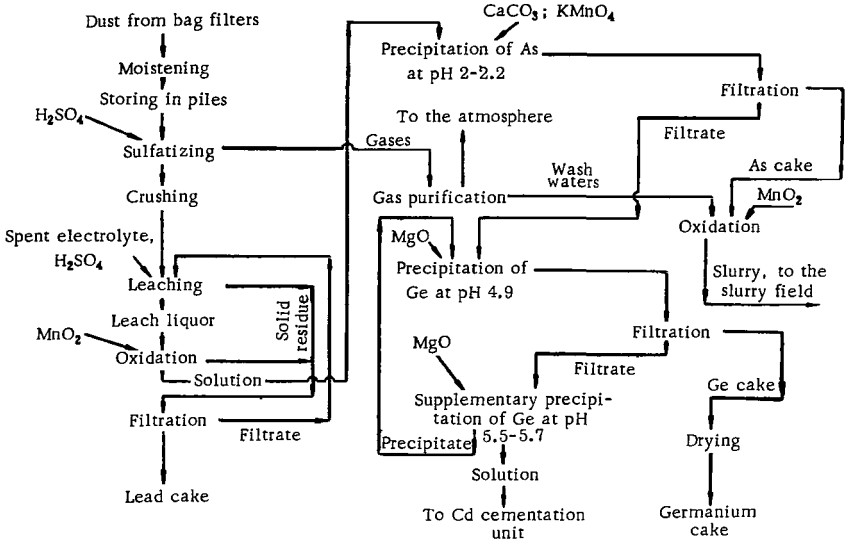

FIGURE 159. Flow sheet of the processing of germanium-containing dusts at the Kolvezi plant in Katanga.

The spent gases (at 250°) are passed through a scrubber, to trap arsenic oxide. The sintered mass withdrawn from the furnace (composition 0.28% Ge, 22.5% Zn, 2.64% Cd, 20.3% Pb, and 0.7% As) is crushed in a hammer mill and leached with a spent sulfate electrolyte in lead-lined reactors, at a solid-to-liquid ratio of $\approx$ 1 : 3. The leach liquor contains 90 to 95% of the Ge, 98 to 99% of the Zn, 94 to 96% of the Cd, 80 to 85% of the As, 75 to 90% of the Cu, and 78 to 80% of the Fe. The acidity of the resulting solution is 10 to 15 g/l H_2SO_4, and it contains 110 to 130 g/l Zn, 15 to 20 g/l Cd, 2.5 to 4 g/l As, 1.4 to 2 g/l Ge, and 2 to 4 g/l Cu.

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In order to separate the arsenic, it is oxidized in advance by adding MnO_2 to the clarified solution, and the oxidation is completed by adding $KMnO_4$. The arsenic is precipitated at pH 2.2 to 2.4 (produced by the addition of limestone), in the form of iron arsenate $FeAsO_4$ and, possibly, arsenates of other elements. The losses of germanium with the precipitate are 3 to 5%. The residual As and Fe concentrations in the solution are only 0.4 and 0.1 g/l respectively.

Germanium is isolated from the arsenic-free solution by a two-stage process with the aid of magnesium oxide. A precipitate richer in germanium (containing magnesium germanate Mg_2GeO_4) is precipitated, first at pH 4.9. It is separated by filtration and the remaining germanium is precipitated at pH 5.5 to 5.7; the precipitate formed is returned to the preceding precipitation. The solutions are neutralized with magnesium oxide. The quantitative precipitation of germanium in the second stage is caused by the precipitation of copper hydroxide, which adsorbs the germanium hydroxide.

The germanium cake taken out of the press filters contains 8 to 10% Ge, 10 to 18% Cu, 15 to 20% Zn, 1 to 1.5% Cd, and 0.7 to 2% As.

The product is treated with hydrochloric acid in order to obtain germanium tetrachloride.

Extraction of germanium from the dust of gas-producing plants /9/

In some cases satisfactory extraction of germanium from the dusts and carbon-black carryovers of gas-producing plants may be obtained by direct processing of the material with hydrochloric acid and the distillation of the $GeCl_4$ formed, or by leaching the dust with sulfuric acid followed by the precipitation of the germanium from the leach liquor.

Germanium may be precipitated from solutions with a low germanium content by using organic precipitants of the tannin type; it is precipitated from solutions of higher germanium content either as germanium disulfide or by cementation on zinc dust.

A satisfactory degree of extraction of germanium from the dust of gas-producing plants cannot always be obtained by direct processing of the dust with acids, since part of the germanium may be bound as compounds which are not decomposed by the acid. In such cases the dusts are decomposed by pyrometallurgical methods: reductive fusion with carbon and fluxes in the presence of copper or iron oxides, or fusion with alkalies.

Reductive fusion. This method is used in England for the extraction of germanium from the dusts of gas-producing plants, containing 0.3 to 1.24% GeO_2 and 0.38 to 0.75% Ga_2O_3. The main dust components are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and Na_2O. A simplified flow sheet of the process is shown in Figure 160. The fusion is carried out in reverberatory furnaces. A molten copper phase is formed during the reductive fusion of the dust in a mixture with copper oxide, carbon, soda ash, quartz sand, alumina, and limestone; the copper contains 90% of Ge and 50 to 60% of Ga. On the average, the alloy contains 3 to 4% Ge and 1.5 to 2% Ga. In addition, arsenic, iron, a fraction of the sulfur and some other impurities also pass into the alloy.

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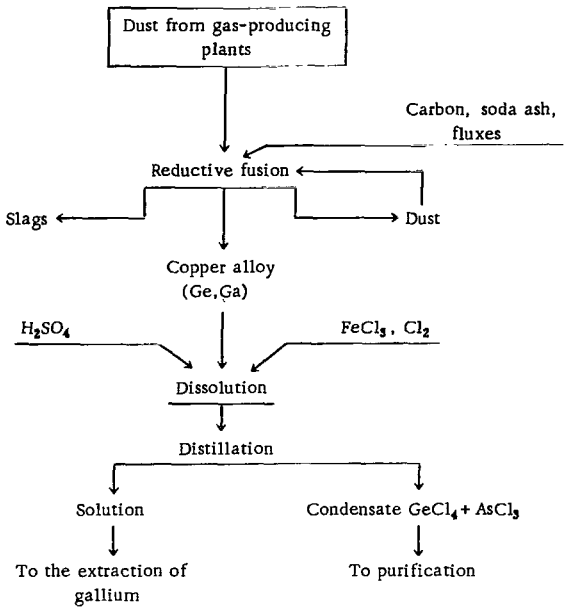

FIGURE 160. Flow sheet of the extraction of germanium from the dust of gas-producing plants, by the reductive fusion method.

The alloy is dissolved in an aqueous solution of ferric chloride while gaseous chlorine is bubbled through it. Ferric chloride acts as catalyst which accelerates the process. The dissolution is carried out in containers made of a fire-resistant glass. Germanium tetrachloride is distilled from the solution. Concentrated sulfuric acid is added dropwise during the distillation process. A part of the nonoxidized $AsCl_3$ and HCl are distilled together with $GeCl_4$. The germanium chloride obtained is taken for purification. Gallium is extracted from the solution remaining after the distillation of the germanium.

Fusion with alkalies. The dust is fused with sodium hydroxide in steel containers and the fused mass is leached with water. The germanium and the gallium (in the form of germanates and gallates) as well as the sodium aluminate and silicate pass into the solution. In order to separate the bulk of the silicon and aluminum, the solution is neutralized with hydrochloric acid to a NaOH concentration of 0.2 N. The precipitate (consisting of silicic acid and aluminum hydroxide) is separated and the solution is neutralized to pH 5. The result is the precipitation of a mixture of germanium and gallium hydroxides. The precipitated hydroxides are dissolved in hydrochloric acid, and germanium disulfide GeS_2 is precipitated from the solution by passing hydrogen sulfide (at an HCl concentration of 4 to 5 N). In other variants of this process germanium is precipitated as magnesium germanate (with the aid of magnesium oxide), which is sparingly soluble in neutral and weakly alkaline solutions.

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81. PURIFICATION OF GERMANIUM TETRACHLORIDE AND PRODUCTION OF GERMANIUM DIOXIDE

The preparation of high-purity germanium (satisfying the specifications for use in semiconductor electronics) requires a thorough purification of all chemical reagents used in the process. Arsenic is the impurity whose removal is of the greatest importance.

Many elements whose chlorides have boiling points higher than that of germanium chloride may be removed from germanium chloride by simple distillation. A thorough purification of germanium chloride is accomplished by rectification or by extraction with hydrochloric acid.

Purification by rectification

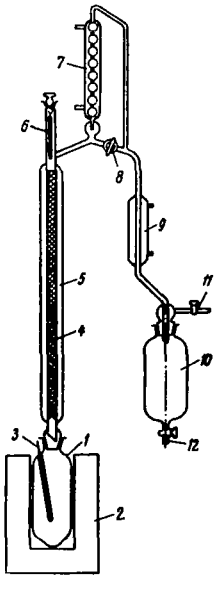

FIGURE 161. Diagram of a rectification column for the purification of germanium chloride.

1—still; 2—thermostat; 3—thermometer; 4—packed column; 5—vacuum jacket serving as thermal insulator; 6—thermometer; 7—still head (condenser); 8—stopcock controlling the withdrawal of distillate; 9—condenser; 10—condensate collector; 11—sleeve connector to the atmosphere; 12—sleeve for the discharge of the condensate.

Germanium chloride is purified by rectification in packed columns. The columns are made of "Pyrex" glass or quartz. A diagram of one such column is shown in Figure 161. The packing used consists of quartz spirals with one loop (the wire diameter is about 1.5 mm, the loop diameter is 4 to 5 mm). A vacuum jacket with a silver-coated inner surface (to reflect the heat rays) serves as thermal insulation of the column.

A column 1220 mm high and 25.4 mm in diameter is equivalent to 40 theoretical plates. The temperature over the length of the column is maintained at about 84°. At the beginning of the operation the column operates without withdrawal of the distillate. The withdrawal of the distillate begins when the temperature reaches 84° over the whole length of the column (about 2% of the distillate is forwarded to the collector while the rest is returned to irrigate the column). The arsenic content in germanium chloride may be reduced to 0.02 to 0.002% by the rectification in a column with quartz packing.

More thorough removal of the arsenic (to a residual content of 0.0001%) is accomplished by prolonged contact of $GeCl_4$ vapors with copper turnings. This causes reduction of the arsenic chloride (by the copper turnings) to copper arsenide Cu_3As_2 which forms a firmly adhering deposit on the copper surface. The chloride vapors are brought into contact with the copper by distilling germanium chloride in a column packed with copper turnings. The column operates under total reflux (i. e., without the withdrawal of distillate) for 12 to 15 hours. The germanium chloride is then distilled into collector bottles /17/.

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Purification by extraction with hydrochloric acid /15/

The removal of arsenic from germanium chloride by extraction with hydrochloric acid is based on the difference in the solubilities of $GeCl_4$ and $AsCl_3$ in concentrated HCl (Table 55).

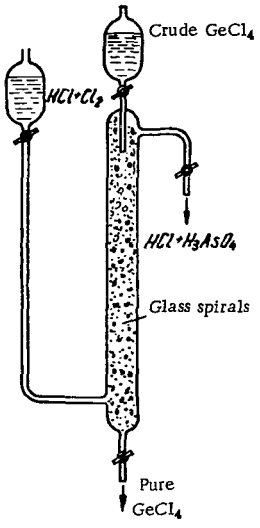

FIGURE 162. Diagram of an extraction column for the removal of arsenic from germanium chloride.

TABLE 55

Solubilities of $GeCl_4$ and $AsCl_3$ in hydrochloric acid at 25°C

HCl concentration, moles/l	Solubility, g/1000 g solution	
	$AsCl_3$	$GeCl_4$
6.80	506	—
7.77	—	85.36
9.52	316.7	—
9.72	—	17.84
15.87	181.5	—
16.14	—	0.882

The effectiveness of the extractive separation is sharply increased by the use of hydrochloric acid saturated with chlorine as the extractant. This is caused by the oxidation of the $AsCl_3$ to arsenic acid:

$$AsCl_3 + 4H_2O + Cl_2 \rightarrow H_3AsO_4 + 5HCl.$$

In order to provide a higher concentration of chlorine in the hydrochloric acid, the saturation with chlorine and the extraction are carried

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out at a low temperature (0° or below). In the case of germanium chloride with a starting As concentration of ~ 0.01 mole %, two extractions with 37.4% HCl (saturated with chlorine) reduce the As concentration to $8.3 \cdot 10^{15}$ atoms As per cm^3 Ge (or $\sim 2.4 \cdot 10^{-5}$ mole % As) while four extractions reduce the As concentration to $6.1 \cdot 10^{15}$ atoms As per cm^3 Ge (or $\sim 1.7 \cdot 10^{-5}$ mole % As).

The extraction may be carried out as a continuous process in a packed column of the type shown in Figure 162. The glass column is packed with glass spirals. The lighter phase (HCl + Cl_2) is fed from the bottom while the heavier phase (the germanium chloride to be purified) is fed from the top. The purified $GeCl_4$ is discharged continuously through a sleeve in the lower part of the column.

Production of germanium dioxide

Germanium dioxide is the main starting material for the production of germanium. The dioxide is prepared by hydrolytic decomposition of purified germanium tetrachloride:

$$GeCl_4 + (2 + n)\,H_2O \rightarrow GeO_2 \cdot n\,H_2O + 4HCl.$$

The water used for the hydrolysis must be very pure in order to prevent contamination of GeO_2 with impurities. The water is purified by passing first through a column with activated carbon (which removes the colloidal and organic contaminants) and then, successively, through columns packed with cation and anion exchange resins which remove the cations and anions. The specific resistance of the purified water is $5 \cdot 10^6$ ohm per cm^3.

The hydrolysis of germanium chloride must be carried out in reactors which are not attacked by the germanium dioxide. In this respect quartz is superior to "Pyrex" glass. The hydrolysis may also be carried out in reactors made of plastic materials such as polyethylene. Germanium tetrachloride is poured (at a predetermined rate) into water, which is taken in an amount such that the resultant HCl concentration after hydrolysis is 5 N. The hydrolysis is rapid at first but then slows down. Several hours mixing is required in order to complete the reaction.

The hydrated germanium dioxide is separated by filtration, washed with purified water and alcohol, and dried at 150 to 200°. Complete dehydration of GeO_2 takes place at that temperature. The drying is carried out in quartz trays placed in electric muffle furnaces.

Precautions used to obtain high-purity germanium dioxide

We have mentioned the need for using corrosion-resistant materials in the purification and hydrolysis of germanium tetrachloride and using high-purity water. In addition, clean rooms and a dust-free atmosphere are of great importance. The air fed to the rooms must be passed through filters. It is recommended that the walls be covered with Dutch tile and the equipment be painted with synthetic paints containing no inorganic pigments.

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82. PRODUCTION OF GERMANIUM /1 — 4, 14/

The most common commercial method for the production of germanium is based on the reduction of germanium dioxide with hydrogen. Another method — the reduction of germanium chloride vapor with zinc vapor — is much more complex and is rarely used.

The overall reaction in the reduction of GeO_2 with hydrogen is:

$$GeO_2 + 2H_2 = Ge + 2H_2O.$$

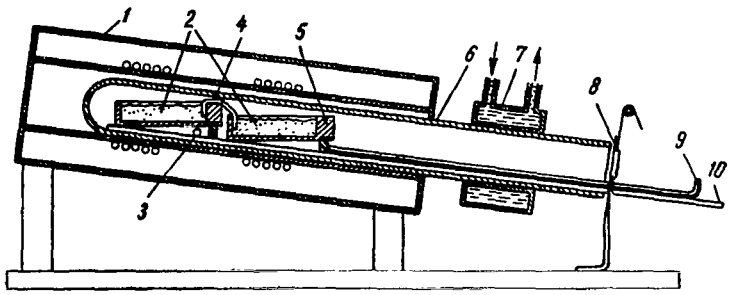

FIGURE 163. Diagram of a furnace used in the reduction of GeO_2 with hydrogen.

1 — furnace; 2 — germanium dioxide; 3 — thermocouple; 4 — graphite rod connecting the boats; 5 — graphite boat; 6 — quartz tube; 7 — cooler; 8 — outlet of hydrogen; 9 — quartz rod for moving the boats; 10 — quartz tube for the supply of hydrogen.

Actually, the reduction is a two-stage reaction, germanium monoxide being the intermediate product:

$$GeO_2 + H_2 \rightarrow GeO + H_2O;$$
$$GeO + H_2 \rightarrow Ge + H_2O.$$

Germanium monoxide is quite volatile above 700°. In order to avoid losses the reduction is carried out at 600 to 685°.

The process is carried out in electrical tube furnaces (with quartz or pure graphite tubes). Germanium dioxide is poured into boats made of dense, high-purity graphite. For a germanium dioxide layer 44 mm thick, the reduction time is 3 to 3.5 hours. After completing the reduction (cessation of the evolution of water vapor), the temperature is raised to 1000° in order to melt the germanium powder. The boat with the molten mass is then withdrawn from the furnace at a given rate. This is the first purification of germanium by the directional crystallization method. The nature of this method is discussed in the next section.

The design of one type of furnace for the batch reduction of germanium dioxide is shown in Figure 163. An electrical tube furnace is fitted with a quartz tube, containing two graphite boats filled with germanium dioxide (about 680 g in each boat). The hydrogen is passed over the boats at a rate of 40 l/min and is ignited at the exit.

The approximate conditions of reduction in batch furnaces is shown in Figure 164. Continuous reduction is carried out in tubular graphite furnaces with different temperature zones. The graphite boats containing germanium dioxide are moved with the tube according to a predetermined

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program and pass first through the reduction zone, then through the germanium melting zone and are finally withdrawn from the furnace.

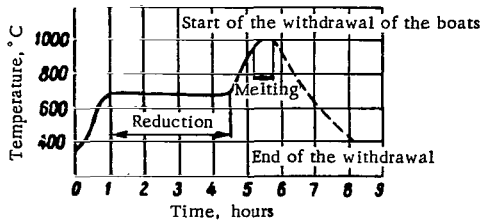

FIGURE 164. Reduction of germanium dioxide and withdrawal of germanium-containing boats from the furnace.

83. PURIFICATION OF GERMANIUM AND PREPARATION OF GERMANIUM MONOCRYSTALS /1—8/

Germanium prepared by the reduction of pure germanium dioxide with hydrogen cannot be used for the manufacturing of semiconductor articles (rectifiers, amplifiers, etc.). Even after very thorough purification, the product is not sufficiently pure. This can be seen from its electrical resistivity, which is usually below 10 ohm·cm. The germanium used in semiconductor electronics must have a resistivity of 40 to 50 ohm·cm, characteristic of germanium with a total impurity content of $\sim 10^{-8}$ to 10^{-9}%, which is virtually impossible to obtain by chemical purification alone.

The required purity is attained by using fractional crystallization methods. The high-purity germanium prepared in this way is then converted into monocrystal germanium bars.

The use of monocrystals yields germanium of standard electrical properties. The existence of grain boundaries in polycrystalline bars, as well as the presence of faults and mechanical stresses in crystals, affect the electrical properties of the semiconductors by interfering with the directed streaming of the charges through the material.

A certain amount of impurities is deliberately added to the germanium during the preparation of the monocrystals in order to obtain germanium of n-type or p-type conductivity with the desired specific electrical resistance.

Thus, the production of germanium with specified electrical properties consists of two stages:

1) purification of germanium by fractional crystallization;

2) preparation of germanium monocrystals with the required electrical properties.

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Purification by fractional crystallization

The purification of metals by fractional crystallization is based on the difference in the solubilities of the impurities in the solid and liquid phases, and on the slow rate of diffusion in the solid phase.

As the crystallization proceeds, solid solution crystals of varying composition crystallize out of the melt. If the contaminant reduces the melting point of the base metal, the first crystals will have a lower content of the contaminant and the contaminant concentration increases in the subsequent crops of the crystals formed. If the presence of the contaminant raises the melting point of the metal (which is less frequent), the first crystals are rich in contaminant and its concentration decreases in subsequent crops. This can be seen in Figure 165, which gives parts of the phase diagram in the range of the solid solutions.

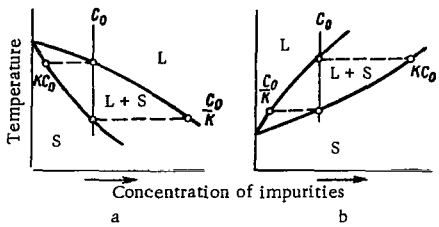

FIGURE 165. Phase diagram segments for the solid solution range.

a—the impurity reduces the melting point of the metal; b—the impurity raises the melting point of the metal; c_0—mean concentration of the impurity in the alloy.

The attainable degree of purification depends on the distribution coefficient $K = c_{solid} / c_{liquid}$, i.e., the concentration ratio of the impurities in the solid and liquid phases. At the average impurity concentration in the alloy (C_0) the impurity concentration in the first infinitesimal volume of solid phase formed would be KC_0. When $K < 1$ (see Figure 165a) $KC_0 < C_0$ and thus the impurity concentration in the crystals would be lower than in the liquid. When $K > 1$ (Figure 165b) $KC_0 > C_0$, i.e., the first crystals formed are enriched with the impurity. The distribution coefficients of a number of impurities in germanium are shown in Table 56. In most cases $K < 1$.

Two methods of fractional crystallization mae use of this effect for the purification of germanium:

1) the directional crystallization method;
2) the zone melting method.

Directional crystallization. The method is illustrated in Figure 166. Germanium is fused in an elongated graphite or quartz boat which is slowly withdrawn from the heated zone. The fusion is carried out in vacuo or in a protective atmosphere (hydrogen, argon, nitrogen).

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TABLE 56

Approximate values of the distribution coefficients of some impurities in germanium

Element	c_{solid}/c_{liquid}	Element	c_{solid}/c_{liquid}
P	0.12	Tl	$4 \cdot 10^{-5}$
As	0.04	Cu	$1.5 \cdot 10^{-5}$
Sb	0.003	Ag	10^{-4}
Bi	$4 \cdot 10^{-5}$	Au	$3 \cdot 10^{-5}$
B	10	Ni	$5 \cdot 10^{-6}$
Al	0.10	Zn	0.01
Ga	0.10	Co	10^{-6}
In	0.001	Si	>1
Sn	0.02		

The concentration of impurities in the bar formed varies over its length. The concentration of impurities which depress the melting point of germanium should increase, while the concentration of impurities which raise the melting point of the metal should decrease in the direction of the crystallization. The distribution of impurities over the length of the bar can be roughly expressed by the equation

$$C_x = KC_0\left(1 - \frac{x}{A}\right)^{K-1},$$

where C_0 is the initial concentration of impurities; C_x is the concentration of impurities at a distance x from the end of the bar; x is the length of solidified section of the bar; A is the total length of the bar; K is the distribution coefficient of impurities between the solid and liquid phases.

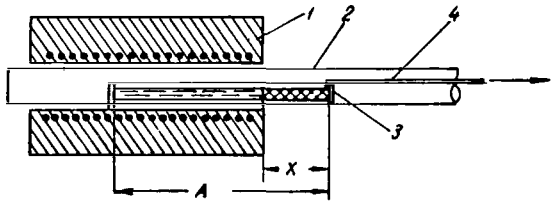

FIGURE 166. Diagram of the purification of germanium by directional crystallization.

1—electric furnace; 2—quartz tube; 3—graphite boat containing the germanium; 4—rod for moving the boat; x—length of the solidified section of the bar; A—total length of the bar.

The equation was derived on the assumption that K is constant, that there is no diffusion in the solid phase, and that the diffusion in the liquid phase is so rapid that the concentration of impurities is the same at any point in the melt. The actual conditions differ somewhat from the ideal.

The distribution of impurities in the bar as a function of the fraction of the bar which has solidified is shown in Figure 167 for different distribution

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coefficients. The curves show that for effective purification the distribution coefficients must differ markedly from unity ($K \ll 1$ or $K \gg 1$). Purification by fractional crystallization is impossible if $K \approx 1$.

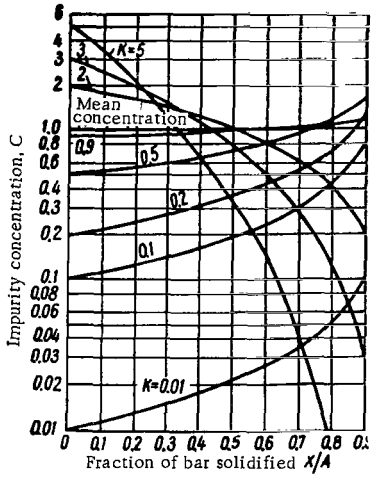

FIGURE 167. Impurity distribution in the bar as a function of the solidified fraction of the bar x/A, at different distribution coefficients. The initial impurity concentration $C_0 = 1$.

The ends of the bar (which are rich in impurities) are cut off and the melting is repeated; this will produce a material of a high degree of purity. However, this method has a number of disadvantages. The yield of purified metal is low since the ends of the bar are removed each time. The process is very time-consuming. Thus, the directional crystallization method is used only for the first purification of germanium and is carried out in the furnace used for the reduction of germanium dioxide.

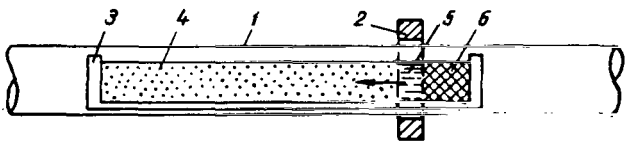

FIGURE 168. Diagram of the zone melting method.

1—quartz tube; 2—ring-shaped heater; 3—boat; 4—germanium bar; 5—molten zone; 6—crystallized section of the bar, past the melting zone.

Zone melting. A diagram of the zone melting method is given in Figure 168. A liquid zone of a width L moves at a given speed along a comparatively long bar of germanium (or a rod made by pressing germanium powder). Thus, only a fraction of the bar (a zone) and not the whole bar, is melted before the start of the crystallization. In contrast

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to directional crystallization, the volume of the melt remains constant until the molten zone reaches the end of the bar.

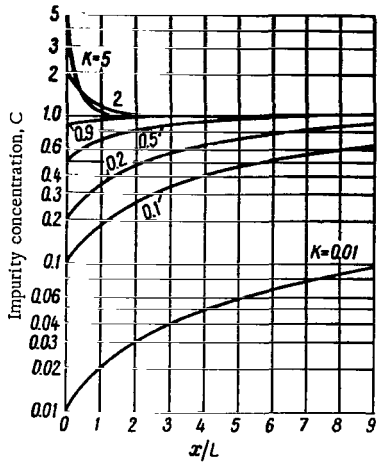

FIGURE 169. Changes in the impurity concentration during the zone melting process, as a function of the x/L ratio at different values of K. Initial concentration $C_0=1$.

Impurities which reduce the melting point of the metal ($K < 1$) move from the starting part (head) of the sample in the direction of movement of the molten zone. If $K > 1$ the dissolved substances (impurities) move in a direction contrary to the direction of the molten zone. The impurity distribution over the length of the bar undergoing purification by zone melting may be approximately calculated by the equation:

$$C = C_0 [1 - (1 - K) e^{-Kx/L}],$$

where C is the impurity concentration in the bar at a distance x from its head; C_0 is the initial impurity concentration; K is the distribution coefficient of the impurities between the liquid and solid phases; L is the width of the zone; x is the length of the solidified section of the bar.

The above equation was derived on the same assumptions as those made in the case of directional crystallization.

Curves showing the variation in the impurity concentration over the length of the bar (the proportion of the solidified section of the bar x/L is given on the abscissa) are presented in Figure 169. The curves are plotted for K values between 0.01 and 5.0 at $C_0 = 1$, for the particular case of a bar of a length $10L$.

For small K values ($K < 0.1$) effective purification may be attained even after a single passage of the zone.

More thorough purification is accomplished by repeated crystallization. For this purpose germanium rod is passed through a number of heaters in series (Figure 170). If, for example, there are six heating zones, one passage of the bar through six molten zones is equivalent to six consecutive

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passages through one zone. In this way a single operation results in several purification cycles without the need for periodic removal of parts of the bar (which is required in directional crystallization).

As is evident from Figure 169, zone melting is not an effective method for the removal of impurities which raise the melting point of germanium ($K > 1$). The best method for the removal of such impurities (e.g., B, Si, see Table 57) is the directional crystallization method.

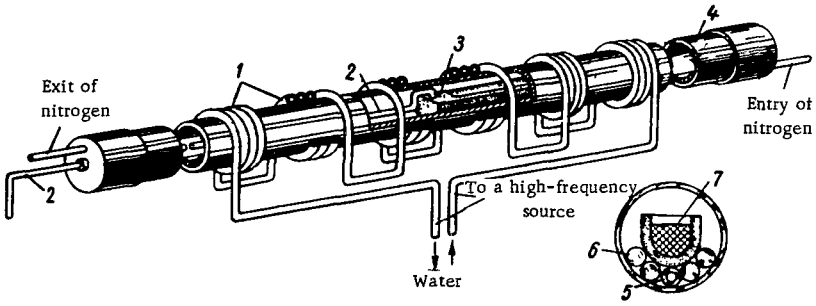

FIGURE 170. Diagram of a zone melting apparatus with several heaters.

1—ring-shaped induction heaters; 2—pulling quartz rod; 3—graphite boat; 4—quartz tube; 5—quartz tube for the supply of nitrogen; 6—quartz rod guides; 7—germanium.

The zone melting of germanium is carried out in a quartz tube containing a quartz or graphite boat with the germanium bar. The diameter of the quartz tube used is 50 to 70 mm, and the boats are 400 to 500 mm long and and 30 to 40 mm in diameter. The distance between the heaters varies from 80 to 150 mm. Ring-shaped resistance furnaces or high-frequency inductors may be used as the heaters. The inductors have a number of advantages: the molten zone is stirred by the eddy currents, and vitrification of the quartz (which is observed upon direct heating to 1100 to 1200°) is prevented.

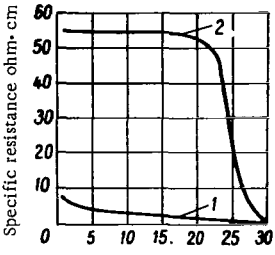

FIGURE 171. Electrical resistance of a germanium bar before and after purification by the zone melting method.

1—before; 2—after zone melting.

The melting is carried out in a vacuum or in a hydrogen or nitrogen atmosphere. In order to avoid diffusion of impurities in the solid bar, it is recommended that the section of metal between two adjacent zones be cooled by ring-shaped coolers. The molten zone is advanced by moving the boat with the germanium or moving the heaters. The length of the molten zone is usually 3 to 5 cm. In the case of longer zones the diffusion may not be sufficient to maintain the same concentration of impurities through the zone. The rate of advancement of the zone ranges from 25 to 350 mm/hr.

A number of passages of a horizontal bar causes changes in its cross section over its length (the bar becomes cone-shaped). Such transfer of material of the molten zone is caused by the changes in the volume of

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germanium upon melting. The decrease in the volume of the melt (as is the case with germanium) causes transfer of matter in the direction of movement of the zone. In order to obtain a bar with a uniform cross section, the quartz tube with the boat is positioned at a certain slope whose angle depends on the ratio of the densities of the solid and liquid phases. In the case of germanium, the slope angle is 2° (the bar end towards which the zone moves is placed slightly higher than the other end).

The effectiveness of zone melting is shown in Figure 171. The specific resistance of germanium bar before zone melting is from 0.3 to 7 ohm · cm. After the zone melting most of the bar has a specific resistance close to the resistance of the pure germanium.

Production of germanium monocrystals /1—4/

The most common method for the production of germanium monocrystals is drawing from the melt (the Chokhralski method).

The process is diagramatically shown in Figure 172. A seed (a small crystal of germanium) fixed on a rod is immersed into molten germanium (at a temperature a few degrees above the melting point) and is then pulled out of the melt at a set rate with the aid of a lifting mechanism. When the seed is pulled out of the melt, the metal solidifies as a crystal with the same orientation as that of the seed. The seed crystal is positioned in a way such that one of its planes (111, 110, or 100) is in parallel to the melt surface. The impurities must be removed from the crystallization front. To do this, the melt is stirred by rotating the crucible and the bar pulled out of the melt. Moreover, rotating the crucible ensures that it is uniformly heated thus preventing local overheating of the molten metal.

There are several types of mechanism for drawing of germanium monocrystals. The melting is carried out in vacuo (10^{-4} to 10^{-5} mm Hg) in pure graphite or quartz crucibles. Either graphite resistance heaters or high-frequency induction heaters are used.

The setup employing a graphite heater (Figure 173) consists of a water-cooled steel cylinder sealed on to a steel plate. The graphite heater is coil-shaped and the current is supplied to it by means of water-cooled conductors passing through the steel plate. The crucible containing the germanium is rotated by means of a rod (joined to its base) passing through the vacuum seal. The cylinder lid is fitted with a window and with a vacuum seal with a rod passing through it. The seed is fixed to this rod. The rod is pulled and rotated at a given rate with the aid of a system of reducing gears activated by DC motors*.

The approximate conditions of drawing are as follows: a vacuum not below 10^{-4} mm Hg is created. The electrical circuit is then closed and the crucible with the germanium is heated to 1100°. The molten metal is allowed to remain for a certain time at that temperature (for degassing), the temperature is then reduced to 965° and the seed is slowly immersed in the melt and allowed to reside in it for a certain time in order to establish good contact between the monocrystal and the melt. The

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* The use of DC motors makes it possible to control the pulling rate by varying the voltage applied to the motors.

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seed-pulling and rotating mechanism is then turned on. At the same time, observations are made through the window in order to ensure that the contact between the crystal and the melt is not broken. Because of the effect of surface tension, the liquid level at the contact site would be higher than the level of the melt. The bar diameter increases as the drawing proceeds. Upon reaching the required diameter, the diameter is kept constant by controlling the supply of heat to the melt and the drawing rate.

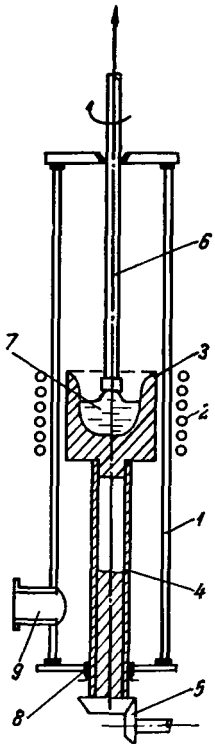

FIGURE 172. Production of monocrystals by drawing from a melt.

1—quartz cylinder; 2—induction heater; 3—graphite crucible; 4—graphite base; 5—mechanism for rotating the crucible and the base; 6—water-cooled rod, with the seed crystal fitted to its end; 7—molten germanium; 8—seal; 9—tube connection to the vacuum system.

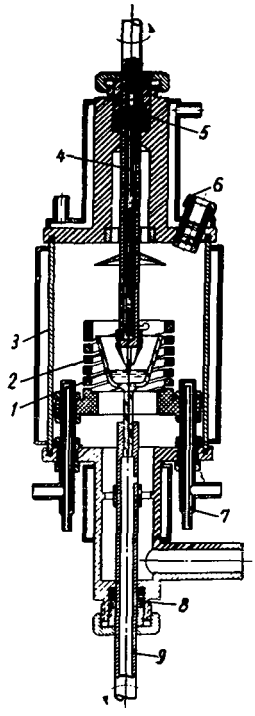

FIGURE 173. Diagram of the setup for drawing germanium monocrystals with a graphite heater /6/.

1—graphite crucible containing germanium; 2—graphite heater; 3—water-cooled steel cylinder; 4—rod, with the seed fixed to it; 5—vacuum seal; 6—window; 7—electrodes supplying the current; 8—vacuum seal; 9—device for rotating the crucible.

In the case of a stationary seed in equilibrium with the melt, the amount of heat supplied to the melt Q_i equals the amount of the heat lost Q_0 (as a result of heat conducted through the seed, and the lifting rod, losses through radiation, etc.). An increase in Q_i must cause an upward shift (i. e., to increase the distance from the melt) of the boundary between

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the crystal and the seed while a decrease in Q_i must cause a downward motion of the crystallization front (i. e., a decrease in the distance between it and the melt surface).

As the seed is pulled out of the melt, the germanium solidifies at a rate S proportional to the difference between the amounts of heat lost and heat supplied $Q_0 - Q_i$:

$$S = \frac{Q_0 - Q_i}{\Delta H d} \text{ cm}^3/\text{sec}$$

where ΔH is the heat of fusion (solidification), cal/g, and d is the density, g/cm^3.

If the pulling rate f (in cm/sec) is constant, the cross section of the crystal will be

$$A = \frac{Q_0 - Q_i}{\Delta H d f} \text{ cm}^2.$$

Hence, the bar diameter is

$$D = \sqrt{\frac{4(Q_0 - Q_i)}{\pi \Delta H d f}} \text{ cm}.$$

The above equation shows that the bar diameter decreases with increasing amount of the heat supplied and with the increasing pulling rate. At a constant pulling rate, the bar diameter may be maintained constant by controlling the amount of the heat supplied. If the pulling rate is varied in accordance with a certain program, these variations must be synchronized with the variations in the melt temperature in order to maintain a constant diameter of the bar. The drawing is controlled automatically.

The germanium monocrystals grown at present are 40 to 50 mm in diameter (occasionally more) and 180 to 220 mm in length.

A strictly controlled amount of admixtures [dopers] is added to the germanium during drawing in order to impart to it the required type of conductivity and the specified resistance. The admixtures (gallium, indium, phosphorus, arsenic, antimony, etc.) are added in the form of an alloy of germanium with the admixture. The concentration of admixtures varies over the length of the bar in a manner similar to that observed in the case of directional crystallization. However, monocrystal sections with a uniform distribution of the admixtures and uniform electrical properties may be obtained by changing the pulling rate as the bar length increases (programmed changes in the rate).

In addition to the drawing method, the zone-melting method is also used for the production of monocrystal bars with a uniform distribution of the alloying additives.

The polycrystalline germanium bar purified by zone melting is placed in a graphite boat. A seed — a monocrystal of germanium — is fixed to the end of the bar. To introduce the admixture creating the required type of conductivity, a pellet of a germanium alloy with that admixture is placed between the seed and the rod. Then, in the same way as in zone melting, a molten zone is formed at the end of the rod, in direct contact with the seed crystal. The zone is moved at a certain rate along the charge, leaving behind it a monocrystal bar.

The admixture (if K is 0.01 or less) is uniformly distributed over a large section of the rod. Such behavior is observed upon the addition of antimony (in the production of n-type germanium) or indium (for p-type germanium).

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The concentration of admixtures after a single passage of the molten zone along the rod can be expressed by the equation:

$$C_s = KC_i e^{-\frac{Kx}{L}},$$

where C_s is the admixture concentration at a distance x from the point at which solidification started; C_i is the initial concentration of the admixture in the molten zone; K is the distribution coefficient; L is the width of the molten zone; and x is the length of the solidified section.

Quality control

In the purification of germanium by fractional crystallization and the production of monocrystals, the quality of the product is controlled by physical methods. The properties usually controlled are*: the conductivity type, specific resistance, and lifetime of minority carriers (which depends on the recombination of electrons and holes in the volume of the semiconductor). In addition the mobility of the charge carriers is determined by measuring the Hall coefficient.

The electrical resistance of the rod is measured over its length without cutting. Rod sections with a specific resistance below 30 ohm·cm are usually returned to additional purification.

84. PROCESSING OF GERMANIUM WASTES /14/

Semiconductor devices (diodes, triodes, etc.) are prepared from monocrystal germanium rods by cutting small plates (say 1·1·0.5 mm). These plates are polished and etched in order to remove the oxide films and contaminants.

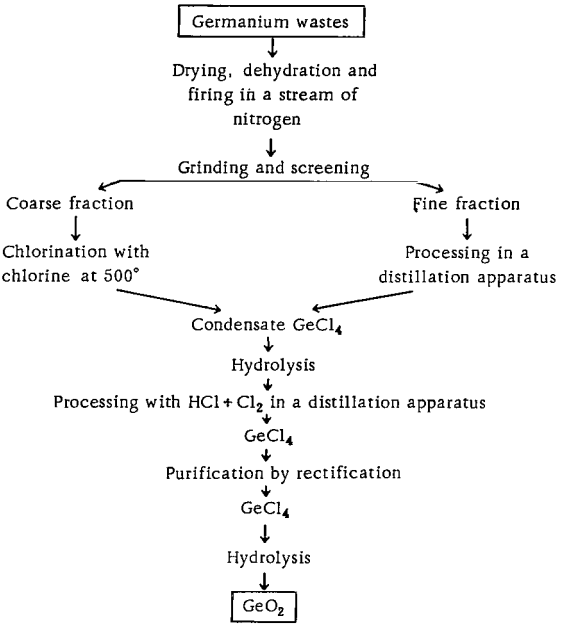

FIGURE 174. Flow sheet of the processing of germanium wastes.

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* A discussion of the nature of these parameters and the methods of their determination is outside the scope of this book. The reader is referred to special textbooks /2-4/.

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The production of these plates is accompanied by the formation of large amounts of waste material: fine dust from the cutting and polishing operations, broken particles, solutions. In practice, not more than 20% of the germanium is obtained as plates which can be used in semiconductor devices, while the remaining 80% is waste.

The dusts and fine particles may be processed as shown in Figure 174. The germanium in the etching solutions and wash liquors is precipitated as mangnesium germanate or as some other compound.

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Chapter VIII

GALLIUM

85. GENERAL DATA ON GALLIUM

Properties of gallium

Gallium was discovered in 1875 by Lecoq de Boisbaudran, who found it by a spectroscopic method in zinc blende.

The properties of this element were predicted with great accuracy as early as 1871 (*i. e., four years before its discovery*) by Mendeleev from his periodic table (see Table 57).

TABLE 57

Properties of gallium as predicted by Mendeleev* and as determined after discovery

Property	As predicted by Mendeleev	As determined after its discovery
Atomic weight	68	69.72
Melting point, °C	Low melting point	29.8
Density, g/ cm^3	5.9	5.9
Atomic volume	11.5	11.7
Oxidation in air	Not oxidized	Slight oxidation at red heat
Decomposition by water vapor	At red heat	At a high temperature
Compound formulas	$EaCl_3$, Ea_2O_3, $Ea_2(SO_4)_3$, $Ea_2(SO_4)_3 \cdot Me_2SO_4 \cdot 24H_2O$	$GaCl_3$, Ga_2O_3, $Ga_2(SO_4)_3$, $Ga_2(SO_4)_3 \cdot (NH_4)_2 \cdot SO_4 \cdot 24H_2O$
Boiling point of the chloride, °C	Volatile	200

* Mendeleev called the element "Eka-aluminum" (Ea) since its properties are analogous to those of aluminum.

Gallium is a soft silvery-white metal. Some of its physical properties are tabulated below:

Atomic number	31
Atomic weight*	69.72
Lattice type and parameter	Rhombohedral, face-centered: a = 4.5167 Å, b = 4.5107 Å, c = 7.6448 Å

* Two natural isotopes of gallium are known: Ga^{69} (60.5% in the mixture found in nature) and Ga^{71} (39.5%).

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Density:	
solid (20°C)	5.904
liquid (29.8°C)	6.095
liquid (1100°C)	5.445
Melting point, °C	29.8
Boiling point, °C	2230
Heat capacity, cal/g °C of:	
solid Ga (0—24°C)	0.090
liquid Ga (29—127°C)	0.098
Heat conductivity at 30°C, cal/cm·sec.°C	0.07—0.09
Linear expansion coefficient:	
solid Ga (0°C)	$1.8 \cdot 10^{-5}$
liquid Ga (100°C)	$12 \cdot 10^{-5}$
Viscosity (in centipoises) at 98°C	1.612
at 1100°C	0.578
Surface tension at 30°C in H_2 or CO_2 atmosphere, dynes/cm	735
Specific electrical resistance, ohm·cm:	
solid Ga (0°C)	$53.4 \cdot 10^{-6}$
liquid Ga (30°C)	$27.2 \cdot 10^{-6}$
Transition temperature to superconducting state, °K	1.1
Normal electrode potential, volts	-0.52
Thermal neutron capture cross section, barns	2.71

Gallium is a liquid with an extended temperature range (30 to 2230°).

The vapor pressures of gallium at 1349 and 1974° are 1 and 400 mm Hg respectively.

Upon rapid cooling, liquid gallium may be maintained in a supercooled state down to -40°. On solidification its volume increases by 3.2%.

Gallium is not attacked by air at room temperature. It is oxidized by dry oxygen above 260°, but the oxidation is very slow since the oxide film protects the metal.

Gallium dissolves slowly in sulfuric and hydrochloric acids, with the evolution of hydrogen. Gallium is not dissolved by nitric acid (of any concentration) at room temperature, but dissolves slowly in the hot acid, through the reaction:

$$Ga + 6HNO_3 = Ga(NO_3)_3 + 3H_2O + 3NO_2.$$

Gallium readily dissolves in hydrofluoric acid. A mixture of HCl + HNO_3 is the best solvent for gallium. It is slowly dissolved by hot alkali solutions, with the formation of sodium gallate $NaGaO_2$ and the evolution of hydrogen.

It should be mentioned that the rate of dissolution of gallium in acids and alkalies decreases markedly with increasing purity of the metal.

Chlorine and bromine react with gallium even in the cold, while iodine reacts on heating.

At temperatures above 300° molten gallium reacts with all structural metals.

The properties of gallium compounds /4, 6, 40/

Gallium belongs to Group III of the periodic system. The most stable compounds are those of trivalent gallium, which in many respects resemble

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the aluminum compounds. In addition, compounds of mono- and divalent gallium are also known.

Gallium oxides. There are two known gallium oxides — Ga_2O_3 and Ga_2O. The dehydration of gallium hydroxide yields the higher oxide Ga_2O_3 — a white substance, insoluble in water. Its density is 6.44; Ga_2O_3 melts at 1740° without decomposition. The heat of formation of Ga_2O_3 is 256 kcal/mole.

Ga_2O is prepared by reduction of Ga_2O_3 with hydrogen at 700 to 800° or by heating Ga_2O_3 with gallium in an inert medium. Ga_2O is dark brown. It undergoes sublimation at 650 to 700°.

Gallium hydroxide $Ga(OH)_3$ is precipitated from solutions of gallium salts as a white gelatinous precipitate. It exhibits distinct amphoteric properties, and, like $Al(OH)_3$, dissolves in both acids and alkalies. On dissolving in alkalies it yields sodium gallate, and on dissolving in acids it yields the respective salts: the sulfate $Ga_2(SO_4)_3$, the chloride $GaCl_3$, etc.

The acidic properties of gallium hydroxide are somewhat stronger than those of aluminum hydroxide. As a consequence, $Al(OH)_3$, is precipitated from solution at pH 10.6 to 4.1 while $Ga(OH)_3$ is precipitated at pH 9.7 to 3.4.

In contrast to $Al(OH)_3$, $Ga(OH)_3$ dissolves not only in strong alkalies but also in ammonium hydroxide. The hydroxide is reprecipitated from the ammoniacal solution upon boiling.

Gallium chloride. Gallium trichloride is a colorless, hygroscopic substance which fumes in air. This is due to the hydrolysis of the chloride upon contact with atmospheric moisture.

$$2GaCl_3 + 3H_2O = Ga_2O_3 + 6HCl.$$

The chloride melts at 78 and boils at 200°. The heat of formation of the chloride is 125 kcal/mole.

Gallium chloride is readily extracted by ethers from hydrochloric acid solutions; this property is used for the separation of gallium from other elements (see Section 88). The reaction of $GaCl_3$ with Ga yields $GaCl_2$ — a colorless crystalline substance melting at 170.5°. The boiling point of $GaCl_2$ is 535°.

Gallium sulfate. A solution of gallium sulfate is formed when gallium hydroxide is dissolved in sulfuric acid. The sulfate crystallizes as the hydrate $Ga_2(SO_4)_3 \cdot 18H_2O$. It is dehydrated on heating and the anhydrous salt decomposes above 520°. Gallium sulfate forms double salts (of the alum type) with alkali metal sulfates, e.g., $KGa(SO_4)_2 \cdot 12\,H_2O$.

Gallium ferrocyanide. $Ga_4[Fe(CN)_6]_3$ is a white, crystalline, sparingly soluble substance. It is precipitated on the addition of potassium ferrocyanide to a solution containing a gallium salt. The precipitation of gallium as the ferrocyanide is used in industry for the separation of gallium from a number of elements: aluminum, chromium, manganese, cadmium, lead, bismuth, and thallium.

Uses of gallium /3/

Gallium is one of the rare metals which have not yet found extensive use in industry. The known reserves of gallium make it possible to produce this metal in amounts much larger than the amounts required today.

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Some of the intended uses of gallium /1 to 3/ are listed below.

Semiconductor electronics is one of the more promising uses of gallium. In this branch, gallium is used as a doper for germanium (gallium imparts to germanium conductivity of the p-type). In addition, some attention has been recently given to the use of intermetallic compounds of gallium (with antimony, arsenic, and phosphorus) which possess semiconductor properties for the preparation of new types of semiconductor devices. The use of gallium antimonide GaSb has been recommended for the preparation of thermocouples (emf = 400 V) and phototriodes which are sensitive to the infrared region of the spectrum.

Nuclear technology. Gallium and its alloys can be used as the liquid medium for the removal of heat in nuclear power reactors. The existence of a liquid phase of gallium metal within a wide range of temperature, its low vapor pressure, and low neutron capture cross section make gallium a valuable heat-transfer material. However, the use of gallium in this field is hindered by the fact that it interacts with most structural materials at the working temperatures used. The materials most resistant to the action of gallium are niobium (up to 400°), tantalum (up to 450°) and tungsten (up to 800°). As compared with gallium, the eutectic alloy Ga — Zn — Sn has a less corrosive effect on metals.

Optical instruments, luminiferous compositions, ultraviolet lamps. Gallium may be used for the production of mirrors with a high reflecting power. Gallium is used as an activator (for the excitation of the fluorescence) in luminescent compositions for lamps and luminescent paints; the amounts used for these purposes is insignificant.

It has been recommended that an aluminum-gallium alloy be used instead of mercury as the cathode in the ultraviolet lamps used in physiotherapy. In that case the radiation emitted by the lamp is enriched with blue and red components, which improves its therapeutic action.

The production of alloys. Gallium forms low-melting alloys with a number of metals: Bi, Pb, Sn, Cd, Zn, In, and Tl. For instance, gallium containing 24% indium melts at 15.7°, gallium containing 12% tin melts at 17°, and the Ga — Tl eutectic mixture melts at 27.8°. These alloys may be used in thermoregulators, sprinkler devices (fire signals) and as substituents for mercury (in rectifiers, current switches, hydraulic seals). They have been recommended as coatings for the working (friction) surfaces of bronze bearings, and may also be used in dentistry (for the preparation of teeth fillings).

It has been recommended that gallium and its low-melting alloys (e.g., the alloy containing 60% Sn, 30% Ga, 10% In) be used as the liquid in high-temperature thermometers (600 to 1300°) and manometers.

86. OCCURRENCE

The abundance of gallium in the Earth's crust is $1.5 \cdot 10^{-3}$% by weight, i.e., the element is more abundant than antimony, silver, bismuth, molybdenum, and tungsten.

Gallium is a typical scattered element. It is found in the form of an isomorphous impurity (at concentrations of 0.04 to 0.001%) in many aluminum and iron minerals and in zinc blende. Only one gallium mineral,

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gallite ($CuGaS_2$), is known (it was discovered in 1958). The mineral germanite has a relatively high gallium content (see Section 78).

The association of gallium and aluminum is based on the similarity of the chemical properties of these elements and on the similarity of their ionic radii (0.57 Å in the case of Al^{3+} and 0.63 Å in the case of Ga^{3+}). As a result, gallium ions may be substituted for aluminum ions in the crystalline lattices of the main commercial aluminum minerals — bauxite and nepheline. The gallium concentration in these minerals ranges from 0.001 to 0.04%.

The association of gallium with zinc is based on the fact that zinc blende ZnS and gallium sulfide GaS are isomorphous, i.e., they have the same crystalline lattice with a parameter $a \approx 5.5$ Å. The gallium concentration in zinc blende is rarely above 0.002%. However, in some cases zinc blende contains 0.1% Ga. In addition to gallium, zinc blende often contains some other scattered metals: indium, thallium, and germanium.

The presence of gallium in some iron ores is attributed to the similarity of the ionic radii of Fe^{3+} (0.67 Å) and gallium.

Gallium occurs in coals together with germanium. Coal ash often contains from 0.01 to 0.1% gallium. In the coal gasification process, the gallium and germanium accumulate in the dusts (the entrained soot). The gallium concentration in the dusts from gas-producing plants is occasionally 0.3 to 0.5%. The accumulation of gallium in the volatile fractions of the ash and the soot is attributed to the volatility of the lower gallium oxide Ga_2O which is vaporized at 650 to 700°.

At present, the wastes of aluminum manufacturing are the main raw material for the production of gallium. In some cases gallium is extracted from the wastes of zinc manufacturing and of gas-producing plants (together with germanium). Gallium is not as yet extracted from iron ores.

Behavior of gallium in the production of aluminum /1, 2, 8 — 13/

Bauxite ores, in which aluminum is present as a component of minerals of the hydrated alumina ($Al_2O_3 \cdot x H_2O$) type, are the most important aluminum raw material.

The production of aluminum from bauxite ores involves two stages: the production of alumina, and the electrolytic production of aluminum from the alumina.

The production of alumina is based on the decomposition of bauxite ores with alkaline reagents, yielding sodium aluminate ($NaAlO_2$) solutions which are then treated to precipitate the hydrated alumina. There are two commercial methods for the processing of bauxites: sintering and leaching in autoclaves (the Baier method).

The first method is based on the sintering of bauxite ore with sodium carbonate and lime, and the subsequent leaching of the sintered mass with water. Aluminum hydroxide is then precipitated from the resulting sodium aluminate solution by bubbling carbon dioxide through the solution (the so-called carbonation method). The precipitates are then fired to yield alumina. The sodium carbonate is returned to the moist mixing of

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the charge components. When nepheline ores (nepheline is $(Na, K)_2O \cdot Al_2O_3 \cdot 2SiO_2$) are used as the raw material, they are also processed by the soda-lime method.

In the Baier method, which was developed in Russia, bauxite ore is processed with sodium hydroxide solutions in autoclaves at 200 to 225°. Aluminum hydroxide is precipitated from the solutions as a result of the hydrolysis (decomposition) of sodium aluminate, and the process is accelerated by the introduction of seeds of freshly-precipitated aluminum hydroxide to the solution:

$$NaAlO_2 + 2H_2O = Al(OH)_3 + NaOH.$$

The mother liquor is evaporated in order to increase the sodium hydroxide concentration and is returned to the leaching of fresh amounts of bauxite.

Both in the first and the second methods, most of the gallium (70 to 80%) accompanies the aluminum into the solution in the form of sodium gallate.

When aluminum hydroxide is precipitated from the solution by the carbonation or the decomposition methods, gallium hydroxide is precipitated after the aluminum hydroxide. This is attributed to the different pH at which the precipitations of $Al(OH)_3$ and $Ga(OH)_3$ from alkali solution begin. As a result the mother liquor from the decomposition process and the last fraction of the precipitate formed in the carbonation process are enriched with gallium.

Thus, in the processing of bauxite containing 0.0025% Ga by the Baier method, the content of Ga_2O_3 in Al_2O_3 in the recycled mother liquors (after the decomposition) is 0.15 to 0.3% i. e., it is 30 to 50 times higher than in the raw material. In the soda-lime method of processing of the bauxites, the solutions taken for carbonation contain about 100 to 120 g/l Al_2O_3 and 0.03 to 0.04 g/l Ga_2O_3. The precipitate formed in the first stage of the process contains 85 to 90% of the Al and at most 20% of the Ga initially present in the solution, i. e., the mother liquor is enriched in gallium. A gallium concentrate is isolated from the mother liquor.

Aluminate solutions are the main raw material for the production of gallium. In addition, gallium may be extracted from the wastes of the electrolytic production of aluminum.

In the electrolytic production of aluminum, gallium is deposited on the cathode together with the aluminum. The gallium concentration in the aluminum is 0.01 to 0.02%. In the refining of aluminum by the three-layer electrolysis method, gallium accumulates in the residual anodic alloy. Its concentration in the anodic alloy may be as high as 0.2%.

87. PREPARATION OF GALLIUM CONCENTRATE FROM ALUMINATE SOLUTIONS

In order to isolate a gallium concentrate in the aluminum production process, it is necessary that gallium be separated from the bulk of the aluminum without necessitating any substantial changes in the bauxite-processing technology. Hence, the methods used for the extraction of gallium depend on the methods of processing of the aluminum raw material.

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Solutions obtained by the soda-lime method /8/

The carbonation is a two-stage process (Figure 175). About 90% of the aluminum is precipitated in the first stage, while most of the gallium remains in the solution. In the second carbonation, the remaining aluminum is precipitated together with the gallium. The Ga_2O_3 concentration in the precipitates (the primary gallium concentrate) is several tenths of one percent.

The precipitates consist of sodium alumocarbonate $Na_2O \cdot Al_2O_3 \cdot 2CO_2 \cdot nH_2O$ contaminated with gallium. In order to separate the bulk of the aluminum from the gallium, the precipitate is treated with lime water at 90° (or at 140° in an autoclave) at a molar $CaO : Al_2O_3$ ratio of 4 : 1. As a result, 60 to 70% of the aluminum is precipitated as tricalcium aluminate while 85 to 90% of the gallium passes into solution from which it is precipitated (by carbonation) as a gallium concentrate containing 2 to 5% Ga_2O_3. The decomposition with lime water is roughly described by the equation:

$$Na_2O \cdot Al_2O_3 \cdot 2CO_2 + 5Ca(OH)_2 + 2H_2O = 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2CaCO_3 + 2NaOH.$$

The formation of sodium hydroxide ensures the retention of the gallium in the solution, provided that the precipitation of aluminum as calcium aluminate is not quantitative. Thus, the amount of CaO taken for the reaction must be smaller than the stoichiometric amount needed.

Solutions from the Baier process

The simplest method involves the isolation of gallium from the recycled solutions of the Baier process by electrolysis on a mercury cathode /10/. This causes no substantial change in the composition of the aluminate solution, which may be returned to the production cycle (Figure 176).

A diagram of the electrolyzer is shown in Figure 177. A hollow rotating iron drum, part of which is immersed in mercury, serves as the cathode. A thin layer of mercury coats both surfaces of the drum. A nickel sieve shaped as a half-cylinder serves as the anode. The anode surface area is 1/20 the area of the cathode.

In aluminate solutions gallium is present as the GaO_2^- anion. Its electrolytic reduction may involve two different mechanisms:

1. The GaO_2^- anions are discharged on the anode with the formation of GaO^+ cations:

$$GaO_2^- - 2e \rightarrow GaO^+ + O.$$

The GaO^+ cations are discharged on the cathode with the deposition of gallium and the formation of the anion:

$$2GaO^+ + 3e \rightarrow Ga + GaO_2^-.$$

2. Hydrogen is evolved on the cathode, reducing the GaO_2^- anions and the GaO^+ cations:

$$GaO_2^- + 2H + e \rightarrow Ga + 2(OH)^-.$$
$$GaO^+ + H + 2e \rightarrow Ga + OH^-.$$

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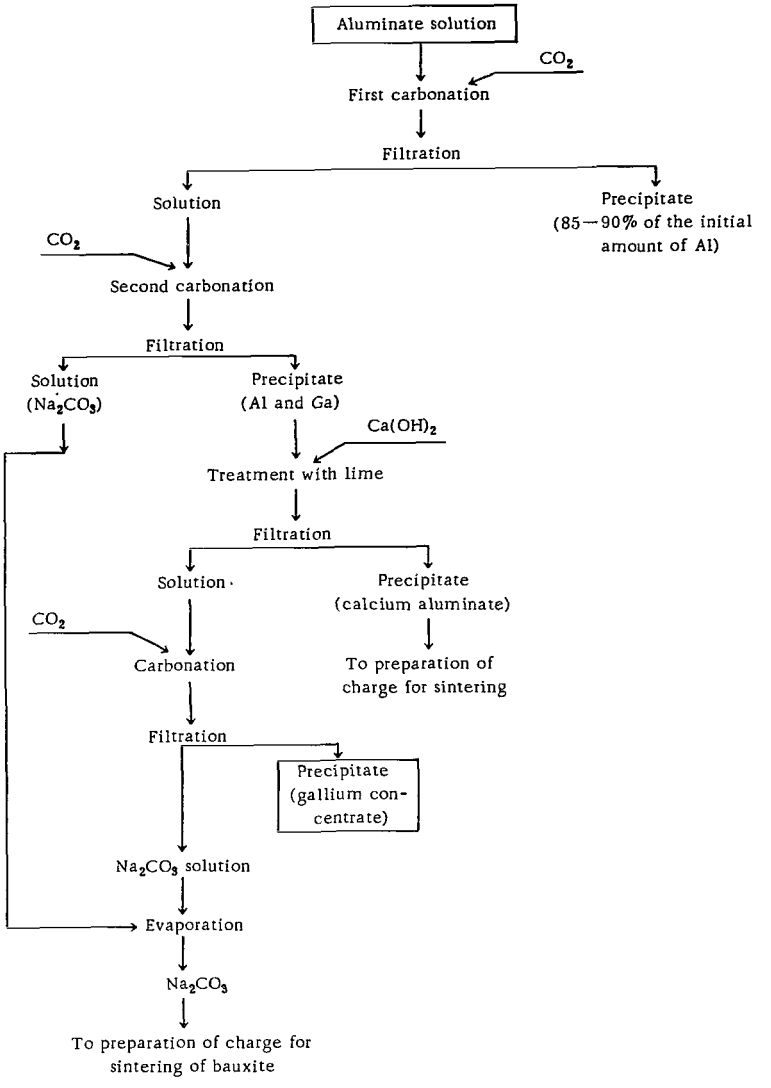

FIGURE 175. Flow sheet of processing the aluminate solution obtained by the sintering method, with gallium as a by-product.

The electrolytic deposition of gallium from aluminate solutions on a mercury cathode requires a close control of the following conditions: mixing rate of the electrolyte and the mercury (accomplished by rotating the drum cathode), current density, temperature, and gallium concentration in the mercury.

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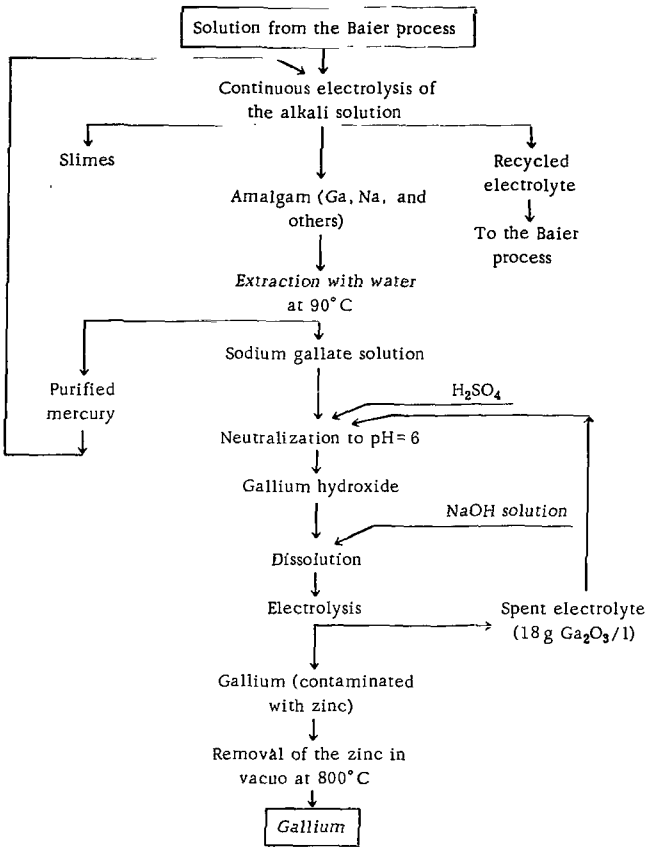

FIGURE 176. Flow sheet of the extraction of gallium in the production of alumina by the Baier process.

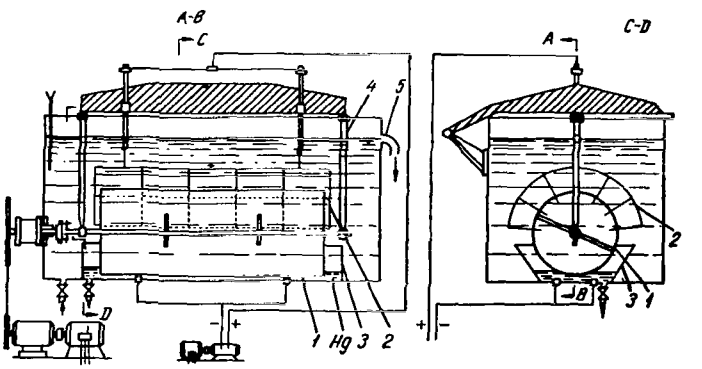

FIGURE 177. Diagram of an electrolyzer for the extraction of gallium from solutions from the Baier process.

1—rotating iron cathode; 2—nickel anode; 3—container with mercury; 4—bakelite support for the axis of the drum cathode; 5—tube for the discharge of the spent electrolyte.

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The optimum conditions for the electrolysis of solutions containing 0.2 to 0.3 g Ga/l are as follows: temperature 40 to 50°, cathodic current density 0.45 amp/dm^2. Under these conditions, the current efficiency is 2.7 to 2.8%. The consumption of electrical energy is about 155 kwh/kg Ga. The electrolysis is continued until the Ga concentration in the mercury reaches 0.3 to 0.4%. Sodium is also deposited on the mercury cathode; under the electrolysis conditions used its concentration in the mercury is 0.1 to 0.2%.

The electrolyte may contain impurities (Mo, Zn, V, Ni, Fe, Mg, Ca). The molybdenum and vanadium are present in the electrolyte as sodium molybdate and vanadate. These two salts are reduced by the hydrogen evolved in the electrolysis, and yield the lower oxides $VO_2 \cdot x\,H_2O$, MoO_2 which are insoluble in alkalies and are precipitated with the slimes. A fraction of the silicon, as well as the zinc, pass into the mercury together with the gallium. Iron, which is present in the alkali electrolyte as a colloidal divalent hydrate, passes quantitatively into the mercury.

The amalgam containing 0.3 to 0.4% Ga is leached with water in a stainless steel reactor heated to 100°. Sodium, being more electronegative, is dissolved first and creates an alkaline solution of a concentration sufficient for the extraction of the gallium. In a boiling alkaline solution the iron is precipitated as the hydrate and is separated by filtration. The resulting gallium solution is not concentrated enough, and thus the gallium is precipitated as the hydroxide by neutralizing the solution with sulfuric acid to pH = 6. The hydroxide precipitate is again treated with sodium hydroxide solution, yielding a sodium gallate solution containing 60 to 80 g Ga/l. From this solution the gallium is isolated by electrolysis (see below).

88. EXTRACTION OF GALLIUM FROM THE WASTES OF THE ELECTROLYTIC REFINING OF ALUMINUM.

The refining of aluminum by the three-layer electrolysis method involves the anodic dissolution of the crude aluminum and the deposition of pure aluminum on the cathode. Pure molten aluminum (density 2.3) serves as the cathode. A mixture containing 60% $BaCl_2$, 23% AlF_3 and 17% NaF (in the molten state its density is 2.7) serves as the electrolyte. Since the electrolyte is denser than the aluminum, it lies beneath the aluminum creating a second layer. The third (lowest) layer is the anodic alloy (crude aluminum containing 25% copper) with a density of ~ 3.5.

Upon electrolysis the aluminum is dissolved at the anode and deposited at the cathode. Elements that are more electropositive (as compared with aluminum), e.g., Cu, Ni, Si, Ga, remain in the anodic alloy.

The anodic alloy (50 to 60% Al, 30 to 35% Cu, 4 to 8% Fe, 1 to 3% Si) is evacuated from the bath after a large amount of impurities has accumulated. The gallium concentration in the alloy is 0.2 to 0.3%. Gallium is extracted from the anodic alloy by methods based on the use of acids or alkalies.

In the method based on the use of alkalies, the anodic alloy is treated with hot alkali solution. As a result aluminum and gallium are dissolved

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while copper and iron remain in the insoluble residue. The gallium may be isolated from the aluminate solution by one of the methods described above. The method based on the use of alkalies has the disadvantages of a low decomposition rate and a low degree of extraction of the gallium into the solution.

The methods based on the use of acids involve the dissolution of the anodic alloy in sulfuric or hydrochloric acids. The gallium, aluminum, and iron are dissolved while the copper remains in the insoluble residue. The gallium may be extracted from the sulfuric acid solutions by precipitation with potassium ferrocyanide or some organic precipitant. The extraction of gallium by ethers from hydrochloric acid solutions is an effective method for freeing the gallium from most impurities.

Precipitation of gallium ferrocyanide

Potassium ferrocyanide $K_4[Fe(CN)_6]$ precipitates gallium from acid solutions, in the form of the sparingly soluble ferrocyanide $Ga_4[Fe(CN)_6]_3$. The aluminum is not precipitated under those conditions. The precipitation is carried out from heated sulfuric acid solutions (H_2SO_4 concentration = 70 to 80 g/l). The white precipitate formed (gallium ferrocyanide) is decomposed with sodium hydroxide solution:

$$Ga_4[Fe(CN)_6]_3 + 22NaOH \rightarrow 4NaGaO_2 + 18NaCN + 3Fe(OH)_2 + 8H_2O.$$

The gallium may be isolated from the solution by electrolysis or by precipitation as the hydroxide (this is accomplished by bubbling carbon dioxide through the solution).

Precipitation of gallium with organic reagents

Some organic reagents precipitate gallium from acid solutions (as a component of an organic complex) while aluminum is not precipitated. Cupferron and sodium diethyldithiocarbamate are such precipitants.

Cupferron is the ammonium salt of nitrosophenylhydroxylamine $C_6H_5 - \underset{\underset{ONH_4}{|}}{N} - NO$. When a 6% solution of cupferron is added to the sulfuric acid solution (1.5 to 2 N H_2SO_4), the gallium is precipitated together with iron and some other impurities (Ta, Nb, Ti, Cu, V). The voluminous precipitate is ignited, yielding a rich gallium concentrate (in which the Ga_2O_3 concentration is $\geqslant 50\%$). The method is costly, because of the high price of cupferron.

Sodium diethyldithiocarbamate $Na[SCS \cdot N(C_2H_5)_2]$ is a less expensive reagent. Aqueous solutions of this reagent precipitate the gallium from cold, weakly acid solutions. As in the case of cupferron, iron, copper and a number of other impurities are coprecipitated with gallium. Aluminum is not precipitated, but a fraction of it is adsorbed on the precipitate.

Gallium is precipitated as a salt — $Ga[SCS \cdot N(C_2H_5)_2]_3$. The precipitate is ignited, yielding a mixture of gallium oxide and the oxides of iron, aluminum, and other elements.

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Purification of gallium compounds by extraction

Ethyl ether readily extracts gallium from hydrochloric acid solutions. The most favorable value of the distribution coefficient is obtained with 5.45 N HCl. In such a case

$$K = \frac{C \text{ ether phase}}{C \text{ aqueous phase}} = 75.$$

The Al, Cr, Mn, Cu, V, and Fe^{2+} ions are for all practical purposes not extracted under these conditions, but Fe^{3+}, Sn and Mo ions cannot be removed by this method. Molybdenum can be separated from a weakly acid solution (pH = 3) by precipitation with hydrogen sulfide (as MoS_3) while tin may be precipitated with hydrogen sulfide from strongly acid solutions.

Gallium is reextracted from the ethereal phase with water or 0.1 N HCl. In some cases, the gallium is isolated by evaporation of the ether in an evaporator with hot distilled water (40 to 50°) instead of by reextraction. The ether is evaporated and gallium chloride is dissolved in water and may be either precipitated as pure gallium hydroxide or deposited by electrolysis from an alkali solution.

Ethyl ether may be replaced by butyl acetate $CH_3-COOC_4H_9$ which is much less flammable (boiling point 126.5°) or by ethyl acetate $CH_3COOC_2H_5$ (boiling point 106°).

89. PRODUCTION OF GALLIUM

Gallium is produced by electrolysis of an alkaline solution of sodium gallate, containing 5 to 100 g Ga/l. The mechanism of the electrolysis has been described above.

Gallium concentrates (oxides or hydroxides) of different degrees of purity may be used for the preparation of the electrolyte. During the electrolysis most of the impurities (elements nobler than gallium) remain in the solution. The electrolysis is carried out at 50 to 60° in baths made of glass, porcelain or organic materials, using stainless steel anodes and cathodes.

The design of one type of bath used in the electrolytic production of gallium is diagramatically shown in Figure 178. Collectors for the liquid gallium are placed on the bottom of the bath beneath the cathodes. The electrolysis is carried out at a bath voltage of 4.5 V and a current density of 0.3 to 0.5 amp/cm^2. The current efficiency (with respect to the yield of gallium) decreases with increasing current density, since this caused an increase in the amount of hydrogen evolved on the cathode. In addition, the current efficiency is strongly affected by the gallium concentration in the solution. At gallium concentrations of 50 to 100 g/l the current efficiency is 45 to 60%, but at a gallium concentration of 2 to 5 g/l the current efficiency drops sharply and is only a few percent. Increasing the alkalinity of the solution also reduces the current efficiency. The metal produced by the electrolysis is washed first with distilled water and then with hot hydrochloric acid. This treatment results in the removal of zinc, copper, lead, iron, and some other metallic contaminants. Successive

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treatments with hydrochloric and nitric acids are occasionally used. The washed metal usually contains 99.9 to 99.95% gallium.

The gallium dissolved by the acid solutions is recovered.

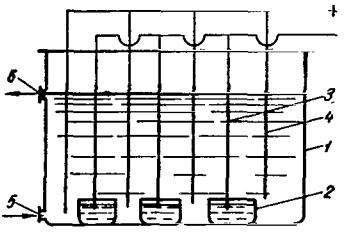

FIGURE 178. Diagram of an electrolyzer for the production of gallium.

1—glass or earthenware bath; 2—gallium collectors; 3—and 4—cathodes and anodes made of stainless steel sheets; 5—tube for the introduction of the electrolyte; 6—overflow of the electrolyte.

Production of very pure gallium /14, 16, 39/

Extremely pure gallium is needed for certain purposes (semiconductor technology, etc.).

Gallium of a high degree of purity (99.9999%) is usually produced by a combination of several purification methods: a) electrolytic refining; b) vacuum distillation of the impurities; c) zone melting.

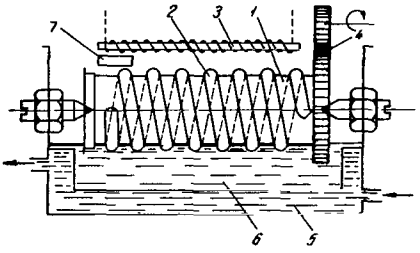

FIGURE 179. Apparatus for purification by zone melting.

1—rotating drum; 2—poly(vinyl chloride) coil filled with gallium; 3—heater; 4—drive gear; 5—cooling liquid (running water); 6—water; 7—shield.

The nature of the zone-melting method was described in the chapter on germanium. Zone melting of gallium is carried out either in a high vacuum or in hermetically sealed tubes filled with gallium. The tubes may be made of poly(vinyl chloride). The liquid gallium crystallizes with some difficulty because of its tendency to supercool. Hence, forced cooling is employed. According to one source /39/, the zone melting is

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conveniently carried out in an instrument (Figure 179) with a rotating drum having a poly(vinyl chloride) tube (filled with gallium) coiled over it. A part of the drum is immersed in water. The rate of rotation of the drum may be regulated between 1/8 and 1 revolution per hour, which corresponds to a zone moving rate of 1.3 to 10 cm/hour. The zones are melted with the aid of a heater placed over the drum, and running water is used as the coolant. The end opposite the direction of movement of the zones is fitted with a shield of aluminum sheet, which accelerates the solidification of the gallium. Gallium of a degree of purity of 99.9999% was produced by using a tube 5 mm in diameter and 100 mm long, the zone moving at a rate of 2 to 4 cm/hour. 99.999% pure gallium was used as the starting material. The yield of the pure metal was about 50%.

Gallium monocrystals are easily produced by drawing from melt. For this purpose the gallium is fused in a quartz crucible heated to 38° in a water thermostat; the sharp edge of a glass tube filled with liquid nitrogen is then immersed in the molten gallium and is withdrawn slowly from the melt. In the drawing process, the bulk of the impurities remains in the residual melt.

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Chapter IX

INDIUM

90. GENERAL DATA ON INDIUM

Indium was discovered in 1863 by Reich and Richter, in the spectroscopic analysis of zinc blende; its name derives from the characteristic blue color of the lines in its spectrum. The new element was at first considered to be an analogue of zinc. Mendeleev corrected the erroneous value of the atomic weight of indium and placed indium in Group III of the periodic table.

The commercial uses of indium date from the twenties and thirties of this century.

Properties of indium

Indium is a soft silvery-white metal of low melting point. Its main physical constants are listed below:

Atomic number	49
Atomic weight*	114.82
Lattice type and parameter	Face-centered tetragonal $a = 4.583$ Å, $c = 4.936$ Å
Density, g/cm^3	7.3
Melting point, °C	156.4
Boiling point, °C	2000—2100
Heat capacity, cal/g°C:	
of solid In (0—150°C)	0.056
of liquid In (155°C)	0.062
Linear expansion coefficient (20°C)	$33 \cdot 10^{-6}$
Specific electrical resistance ohm·cm:	
of solid In (0°C)	$8.2 \cdot 10^{-6}$
of liquid In (155°C)	$29 \cdot 10^{-6}$
Brinell hardness, kg/mm^2	~1.0
Modulus of elasticity, kg/mm^2	1100
Tensile strength, kg/mm^2	0.23
Normal electrode potential, V	-0.34
Thermal neutron capture cross section, barns	190
Transition temperature to the superconducting state, °K	3.37

* Natural indium consists of two isotopes: In^{113} (4.33%) and In^{115} (95.67%).

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Virtually no work hardening of indium is observed upon mechanical (pressure) working of the cold metal since the metal recrystallizes even at room temperature.

Solid indium is not attacked by air, but it is oxidized above the melting point, yielding the oxide In_2O_3. The solid metal is virtually not corroded by water and alkaline solutions. Indium powder or sponge are oxidized slowly in water in the presence of oxygen, yielding indium hydroxide.

Indium dissolves slowly in dilute inorganic acids at room temperature, and more rapidly upon heating. The metal dissolves readily in concentrated inorganic acids.

Indium is not dissolved by acetic acid, but it reacts with oxalic acid as follows:

$$2In + 6H_2C_2O_4 = 2H_3[In(C_2O_4)_3] + 3H_2.$$

The properties of indium compounds /17, 40/

Indium forms compounds in which it is mono-, di- and trivalent. The compounds of trivalent indium are the most characteristic.

Indium oxide and hydroxide. Indium oxide In_2O_3 is a yellow powder with a melting point of $\approx 2000°$. It is practically insoluble in water, but readily dissolves in acids. It is formed when indium is heated in air, or upon ignition of indium hydroxide $In(OH)_3$, nitrate, carbonate, or other indium salts. The density of In_2O_3 is 7.18.

The heat of formation of In_2O_3 is 220.5 kcal/mole. In_2O_3 dissociates above 750°, yielding In_3O_4.

Indium oxide is reduced to the metal by hydrogen or carbon at 700 to 800°. The lower oxides InO and In_2O are intermediate reduction products. In_2O has an appreciable vapor pressure above 800°.

Indium hydroxide ($In(OH)_3$) is amphoteric but its acidic properties are less strongly exhibited as compared with gallium hydroxide. For instance $In(OH)_3$ dissolves in cold solutions of sodium hydroxide, but is precipitated when the alkaline solution is heated. In contrast to $Ga(OH)_3$ indium hydroxide is insoluble in solutions of ammonium hydroxide. Indium sulfate, chloride and nitrate are hydrolyzed in solutions at pH above $\sim$ 3.5 to 3.7, with the precipitation of indium hydroxide or basic indium salts.

Indium chloride $InCl_3$ is a colorless volatile substance. The vapor pressure of $InCl_3$ over the solid salt is one atm at 498°. Under pressure the chloride melts at 586°. The salt is readily soluble in water and its solubility at 22° is 33.5 g/l. Solutions of $InCl_3$ are formed upon the dissolution of In_2O_3 or metallic indium in hydrochloric acid.

Indium sulfate $In_2(SO_4)_3$ is a water-soluble salt (62.1% at 25°). From neutral solution it crystallizes as the pentahydrate $In_2(SO_4)_3 \cdot 5H_2O$. It slowly loses water at 100 to 120° and is converted to the anhydrous salt. Depending on the sulfuric acid concentration and the temperature, it is precipitated from acid solutions as $In_2(SO_4)_3 \cdot 10H_2O$, $In_2(SO_4)_3 \cdot 6H_2O$, or the acid salt $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ which may be regarded as a complex salt with the formula $H[In(SO_4)_2] \cdot 3\frac{1}{2} H_2O$ (see Table 58).

The solubility of indium sulfate is strongly affected by the sulfuric acid concentration. At H_2SO_4 concentrations above 55% the solubility of indium

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sulfate is only 0.5% and the acid salt is precipitated from the solution. The precipitation of indium from sulfuric acid solutions by "salting-out" with sulfuric acid may be used as a means for the purification of indium.

TABLE 58

Solubility of $In_2(SO_4)_3$ as a function of the sulfuric acid concentration

At 20°			At 60°		
H_2SO_4 concentration, %	Solubility of $In_2(SO_4)_3$, %	Composition of the solid phase	H_2SO_4 concentration, %	Solubility of $In_2(SO_4)_3$, %	Composition of the solid phase
3.6	51.19	$In_2(SO_4)_3 \cdot 10H_2O$	2.9	54.80	$In_2(SO_4)_3 \cdot 6H_2O$
10.3	40.81		10.6	44.56	
20.2	30.44		14.2	39.24	
25.3	24.80		22.5	28.86	
28.2	21.58	$In_2(SO_4)_3 \times H_2SO_4 \cdot 7H_2O$	36.7	12.65	
30.8	18.94		43.5	6.71	
41.3	6.51		52.8	2.05	
49.7	1.75		54.4	1.62	$In_2(SO_4)_3 \times H_2SO_4 \cdot 7H_2O$
53.4	0.75		60.6	0.61	
54.9	0.55		68.0	0.37	
90.2	0.07		84.4	0.13	

Indium sulfides. Trivalent indium may be precipitated from weakly acid solutions (0.03 to 0.05 N) in the form of the yellow sulfide In_2S_3; in some manufacturing processes this reaction is used to separate indium from iron. The sulfide In_2S_3 melts at 1050° and undergoes noticeable sublimation above 800°. When heated in a current of hydrogen, In_2S_3 is reduced to a black sulfide of monovalent indium:

$$In_2S_3 + 2H_2 = In_2S + 2H_2S.$$

Alkali metal sulfides form soluble double salts with In_2S_3 such as $NaInS_2$.

Indium phosphate and arsenate are sparingly soluble in water and in weakly acid solutions (pH $\approx$ 2 to 3).

Uses of indium

Indium is extensively used in industry. This is indicated by the total output of indium which reaches about 30 to 35 tons/year in the countries outside the USSR /29/.

Coatings. Until recently indium was used mainly for protective coatings against corrosion (e.g., coating aircraft bearings to protect them against attack by the hot lubricating oils). Indium coatings are applied by electrodeposition. Usually, the indium-plated part is heated after the plating to a temperature slightly higher than the melting point

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of indium. This causes the diffusion of indium into the surface layer and makes the coating adherent. Indium coatings have a high reflectance. In contrast to silver coatings they do not darken and retain their reflectance coefficient. Hence, indium is used in the manufacturing of reflectors.

The production of alloys. Some indium alloys with lead, tin, silver, cadmium and bismuth are of importance for technology. The In — Sn — Cd — Bi, In — Pb — Sn, and In — Pb alloys are used as solders for joining metals, glass, quartz, and ceramics. Indium-tin alloy (50% In, 50% Sn) solders are used in vacuum technology for making glass-to-glass or glass-to-metal joints. These solders produce vacuum-tight joints. Low-melting alloys containing indium are used in fire alarms. One of these alloys contains 18.4% In, 40.7% Bi, 22% Pb, 10.6% Sn, and 8.16% Cd. It melts at 46.5°.

An alloy containing 19% In, 71% Ag, and 10% Cd is cheaper than hafnium and is being used recently in the USA for the production of control rods for nuclear reactors. This alloy is characterized by its high thermal conductivity, corrosion resistance, and strength, and its thermal neutron capture cross section is sufficiently high. An alloy containing 54 to 62% In, 8 to 18% Cd, and the balance bismuth has also been proposed as a neutron-absorbing material.

Semiconductor electronics. A large fraction of the indium produced is used at present in semiconductor electronics. Both pure indium and indium compounds are used in this field.

Very pure indium is used in the production of high-power germanium rectifiers. The presence of indium imparts to germanium a p-type conductivity. The indium is fused on the surface of germanium plates. The indium atoms diffuse into the germanium surface and create a zone with p-type conductivity.

A number of indium compounds (oxide, sulfide, selenide, telluride, antimonide, arsenide, etc.) have semiconducting properties. They may be used in thermocouple materials. For instance, thermocouples made of indium arsenide or phosphide may operate at high temperatures.

The indium and indium compounds used in semiconductor electronics must be of a very high degree of purity. Thus, attention has been recently given to the development of indium-refining methods.

91. OCCURRENCE

The concentration of indium in the Earth's crust is 10^{-5}% by weight. There are no indium minerals. Increased concentrations of indium have been found in sulfide minerals (mainly in zinc blende) and in minerals composed of lead and zinc sulfostannates and sulfoantimonates.

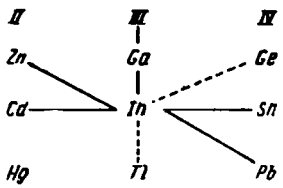

FIGURE 180. The geochemical "star" of indium.

The highest concentrations of indium have been found in the following minerals: cylindrite $Pb_6Sb_2Sn_6S_2$ (from 0.1 to 1% In), franckeite $Pb_5Sb_2Sn_2S_{12}$ (up to 0.1% In), and stannite $CuFeSnS_4$ (up to 0.1% In).

The indium concentration in sphalerites (zinc blendes) fluctuates between 0.1 and 0.0001%. The higher indium concentrations are found in zinc deposits of increased iron and tin contents.

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The position of indium in the periodic table (Figure 180) explains to a certain extent its geochemical association with a number of elements. The association with cadmium and tin is caused by the similar values of the atomic radii of indium and these elements; the association with zinc and lead is attributed to the known similarity in the properties of elements positioned diagonally in the periodic table; the association with gallium and aluminum is due to the fact that indium and these elements belong to the same group.

The various waste materials and intermediate products of zinc and lead manufacturing are the main sources of indium. In addition to indium, these products often contain cadmium and some rare scattered metals: gallium, thallium, and germanium.

Attention has been recently given to the extraction of indium from the wastes of production of tin.

The behavior of indium in the various stages of zinc and lead manufacturing processes, and the methods of extracting indium from the waste materials of these processes are discussed below.

92. BEHAVIOR OF INDIUM IN THE PRODUCTION OF ZINC AND LEAD /23, 30/

In the oxidative roasting of zinc concentrates (carried out at 850 to 930°) most of the indium remains in the zinc cinders. The cinders may then be processed by hydrometallurgical or pyrometallurgical methods.

Pyrometallurgical production of zinc

The pyrometallurgical method for the production of zinc involves the reduction of zinc cinders (zinc oxide) with carbon in retort furnaces at 1200 to 1300°. The zinc is distilled during the reduction process (it has a bp of 900°) and is collected in condensers as liquid zinc.

Prior to the reduction in the retort furnace, the mixture of zinc cinders with coal is subjected to agglomerative roasting in sintering machines at 1100 to 1200°, or the mixture is pelletized and the pellets are coked at 900 to 1000°. A small fraction of the indium is volatilized during the agglomerative roasting. When pelletizing and coking are used instead of agglomeration, a fraction (about 20%) of the indium is volatilized (as In_2O and InO) during the coking and accumulates in the dust.

About 60 to 70% of the indium is distilled together with the zinc during the reduction of the agglomerate or pellets in the retort furnace. This is attributed to the fact that at 1200 to 1300° indium has an appreciable vapor pressure (about 0.8 to 1 mm Hg). Ten to fifteen percent of the indium remain in the retort residues and the rest is distributed between the other distillation products (dusts). The crude zinc contains 0.002 to 0.007% In, depending on the In concentration in the starting concentrate.

During the refining of crude zinc in rectification columns, indium (which has a high boiling point) accumulates in the lead fraction (in the "lead" column), from which it may be extracted during the refining of the lead.

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Thus, in pyrometallurgical production of zinc, indium is extracted from the dusts of pellet coking furnaces and from the lead produced in the rectification of crude zinc.

Hydrometallurgical production of zinc

The hydrometallurgical production of zinc involves the leaching of zinc cinders with dilute sulfuric acid, the removal of impurities (copper, cadmium, cobalt and chlorine) from the sulfate solutions, and the electrolytic deposition of zinc from the solutions. The cinders are leached in two stages: neutral leaching and acid leaching (Figure 181).

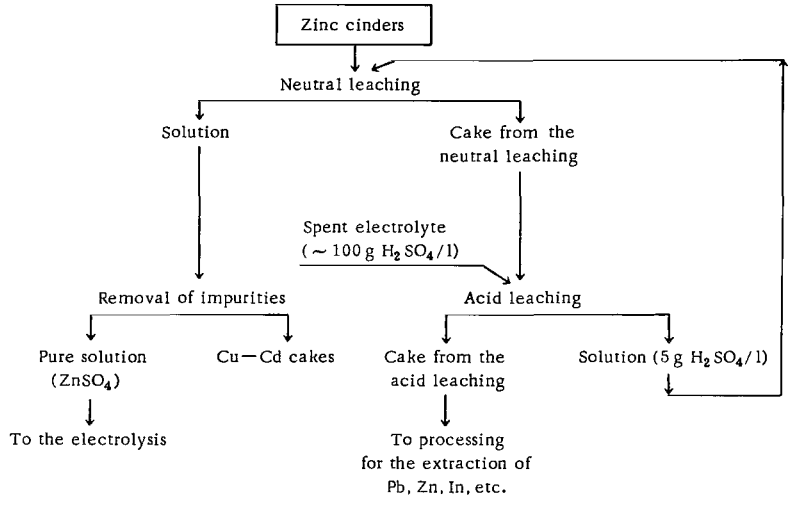

FIGURE 181. Flow sheet of the hydrometallurgical production of zinc.

During the leaching most of the indium remains in the insoluble residue — the zinc cake. This is attributed to the fact that in the neutral leaching the leaching is continued until the solution reaches a pH of 5.2 (which corresponds to the beginning of zinc hydroxide precipitation). Quantitative precipitation of indium hydroxide takes place at pH 4.67 to 4.85.

The hydrated oxides of iron, gallium, germanium, and other elements also concentrate in the cakes from the neutral leaching. In the acid leaching, the zinc is the first to be extracted into the solution since it is the main component of the precipitate. As a result the bulk of the indium, gallium, germanium, and other components remain in the cake together with the lead sulfate.

For some unknown reason, a fraction of the indium always remains in the sulfate solutions from the neutral leaching, which explains the presence of indium in the copper-cadmium cakes produced as a result of the removal of copper and cadmium from the solution by cementation on zinc dust.

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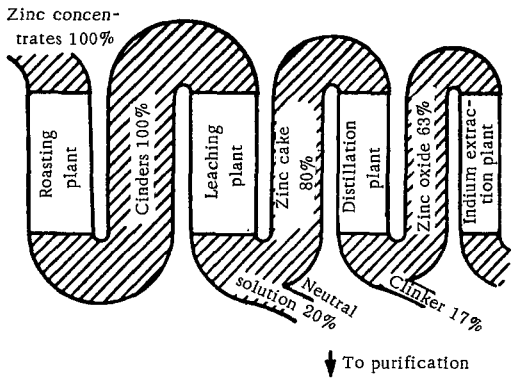

FIGURE 182. Distribution of indium between the zinc concentrate-processing products /30/.

Most of the zinc cakes are processed by distillation of the oxides from the solid cake (the rotary-kiln process) or from the liquid slag (the fuming process).

The condensed distillates (the oxides of zinc, lead, cadmium, and other elements) usually contain 40 to 65% Zn, 4 to 8% Pb, and 0.3 to 0.4% Cd. The scattered metals — indium, gallium, and germanium — also concentrate in the condensates. The indium concentration in the distillates (oxides) ranges from a few thousandths to a few tenths of one percent.

The indium concentration in the copper-cadmium cakes is of the same order of magnitude; the indium may be extracted from these cakes as a by-product of cadmium manufacturing.

The distribution of indium in the products of the hydrometallurgical processing of zinc concentrates is shown in Figure 182.

The above data show that in the hydrometallurgical production of zinc the indium may be extracted from the distillates of the rotary-kiln or fuming processes and from the copper-cadmium cakes.

Production of lead

The lead-production process includes the following main stages:

1) agglomerative roasting of lead concentrates in sintering machines;
2) smelting in shaft furnaces, which yields crude lead and slags;
3) refining of the crude lead.

Only a small fraction of the indium is volatilized during the agglomerative roasting in sintering machines. During the smelting in shaft furnaces the indium is distributed almost evenly between the lead and the slags. A fraction of the indium remains in the dusts. The approximate distribution of indium during the shaft-furnace smelting is shown in Table 59.

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A fraction of the slags formed in the lead smelting is returned to the agglomeration process. The rest of the slags is usually taken for rotary-kiln distillation in which the indium is distilled together with zinc and lead.

TABLE 59

Distribution of indium and indium concentration in the various products of shaft-furnace smelting of lead at a plant /30/ in the USSR

Smelting product	In concentration,%	Fraction of the total amount of In,%
Crude lead	0.001—0.002	30—35
Slags	0.001—0.0015	40—45
Dusts	0.008—0.01	20—25
Circulating products: matte, slags and scrapings.....	0.0015—0.002	5

The crude lead is processed to successively remove copper (by liquation and treatment with sulfur), zinc (by oxidation with air which yields the oxides, the so-called drosses), and the other contaminants. In the lead-refining process most of the indium (80 to 90%) accumulates in the copper skimmings and oxides (drosses) removed from the surface of the liquid lead. The indium concentration in these products ranges from several hundredths to several tenths of one percent.

The copper skimmings are usually smelted in reverberatory furnaces. The smelting yields crude lead, matte (mainly copper sulfides), slags, and dusts. The indium present in the copper skimmings is distributed among all smelting products, the highest concentrations being in the dusts (0.1 to 0.4%) and slags.

Thus, in the production of lead indium may be extracted from the lead-refining products (copper skimmings, oxides) and from the various products of their processing (e.g., the dusts and slags from the reverberatory smelting of copper skimmings).

93. EXTRACTION OF INDIUM FROM INDIUM-ENRICHED PRODUCTS

The products that serve as the raw materials for the extraction of indium differ in their indium contents and in the concentrations of their main components: zinc, lead, etc. Thus, the distillates (oxides from rotary-kiln distillation) from the processing of zinc cakes and the slags from lead smelting, as well as the skimmings from the oxidative refining of lead are composed mainly of the oxides of zinc, lead, cadmium, and some other metals. The copper-cadmium cakes are composed primarily of metals. They contain copper, lead, zinc, indium, thallium, etc.

Indium concentration in the above products ranges from a few thousandths to a few tenths of one percent. The indium extraction processes usually involve two stages:

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1) the production of an indium concentrate containing at least 1 to 2% In;
2) the production of crude indium.

Production of indium concentrates

Indium is dissolved by leaching the starting material with sulfuric acid; the leaching is usually a two-stage process. Neutral leaching is carried out first (pH of ~ 5.2 is reached at the end of the dissolution); it results in the extraction of the bulk of the zinc while the indium remains in the insoluble residue.

Acid leaching is then carried out and the indium is dissolved. The bulk of the lead remains in the insoluble residue, as $PbSO_4$.

TABLE 60

pH of precipitation of the hydroxides of some elements

Element	Valency of the ion	pH of precipitation
Zinc.....	2	5.2—6.5
Iron	2	5.5—7.5
Iron	3	2.5—3.0
Aluminum.....	3	4.1—5.0
Gallium	3	3.4—4.5
Indium	3	3.5—4.8
Thallium	3	3—3.5
Copper.....	2	5.5—6
Cadmium	2	8
Tin	2	2—3
Tin	4	0.45—2

Occasionally, preliminary sulfatizing of the material is carried out in order to obtain a higher degree of extraction of the indium. For this purpose the material is mixed with concentrated sulfuric acid, the mixture is heated to 300 to 500°, and the sulfatized material is then leached with water. During the sulfatizing roasting the arsenic is removed in the form of As_2O_3.

In order to concentrate the indium it is necessary to separate it from the bulk of the main components (Zn, Pb, Cu, Cd, Fe, and Al). The first processing stage is usually based on the hydrolytic method which makes use of the different pH of precipitation of indium hydroxide and the hydroxides of the other elements — zinc, cadmium, copper, and aluminum (see Table 60).

The bulk of the zinc, copper, and cadmium may be separated from the indium by regulating the pH of the solution. Precipitates enriched with indium are obtained by repeating the dissolution and neutralization stages. The solution is neutralized with zinc oxide.

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The primary concentrates prepared by hydrolytic precipitation are subsequently processed by various methods (selective dissolution and precipitation, and cementation*).

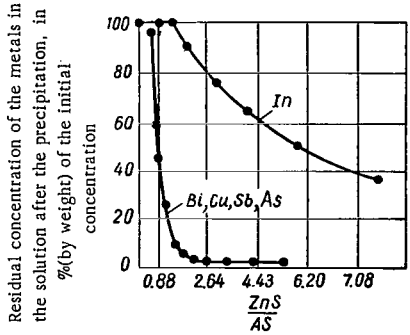

FIGURE 183. The concentration of contaminants in solution after the precipitation of the sulfides, as a function of the amount of the precipitant (ZnS) used.

Selective dissolution and precipitation methods.

1. Processing of the hydroxide precipitates with hot solutions of sodium hydroxide, leading to the extraction (into the solution) of aluminum, gallium, germanium, zinc, and lead as the respective sodium salts (aluminate, zincate, plumbite, etc.).

2. Treatment of the indium-containing solutions with an excess of ammonia. The indium, iron, and aluminum are precipitated as the hydroxides while the zinc, copper, and cadmium remain in the solution as complex ammonium salts $[Me(NH_3)_4](OH)_2$.

3. Precipitation of indium arsenate or phosphate in a weakly acid medium (pH $\approx$ 3.7 for arsenates and $\approx$ 3.2 for phosphates). The bulk of the zinc, cadmium, lead, and divalent iron (trivalent iron must be reduced in advance) remains in solution. The arsenate or phosphate precipitates are then decomposed with an alkaline solution, yielding indium hydroxide.

4. Precipitation of impurities (bismuth, copper, antimony, and arsenic) as the sulfides. When ZnS is added to the indium solution, the sulfides of the above elements are precipitated at first (Figure 183), and the indium is bound afterwards. By using a predetermined amount of ZnS the sulfides of the impurity elements may be precipitated without losing indium. The use of zinc sulfide as a precipitant eliminates the introduction of other ions (e.g., Na^+ if Na_2S were used).

Selective cementation methods. The cementation process is based on the displacement of a metal from a solution of its salt by a more electronegative metal. The normal potentials of the elements are, in volts:

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* It is of interest to mention a recently developed method for the extraction and purification of indium by extraction with alkylphosphoric acids /21/.

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Al/Al^{3+}	−1.53
Zn/Zn^{2+}	−0.76
Ga/Ga^{3}	−0.52
Fe/Fe^{2+}	−0.44
Cd/Cd^{2+}	−0.40
In/In^{3+}	−0.34
Tl/Tl^{+}	−0.336
Ge/Ge^{4+}	−0.15
Sn/Sn^{2+}	−0.136
As/As^{3+}	+0.247
Cu/Cu^{2+}	+0.34

As is evident from the above table, indium as well as some other metals may be precipitated by cementation on zinc, which has a low normal potential (-0.76 V). Zinc dust is commonly used for the cementation of impurities. The use of a predetermined amount of zinc dust permits the precipitation of copper while indium and other less noble metals remain in the solution. Iron may also be used for the selective cementation of copper. When copper is precipitated by cementation on iron, the arsenic is also precipitated as the arsenide Cu_3As_2. After the copper has been separated, the indium together with a fraction of the cadmium is precipitated by cementation on zinc. As a result, the indium is separated from the bulk of the iron and aluminum in the solution.

The amalgam method /31/ based on the extraction of the indium and a fraction of the impurities into a zinc amalgam has recently found extensive use. The indium is extracted from the amalgam by anodic (electrolytic) dissolution and cathodic deposition.

The amalgam method is based on the marked solubility of some metals in mercury (In ~ 75%, Tl ~ 45%, Ga ~ 2%) and the strict sequence of transport of the metals from the solution into the amalgam and from the amalgam into the solution, on the stability of the amalgams in aqueous solutions and the absence of chemical interaction between the metals and the mercury, on the large density of mercury and the amalgams, which makes it possible to concentrate large amounts of the metal (indium) in a small volume of the amalgam (about 10 kg of indium may be concentrated in one liter of mercury).

Production of crude indium

Crude indium is precipitated from the purified solutions by cementation on zinc or aluminum sheets. The rate and degree of completion of the cementation of indium depend on the sulfuric acid concentration (SO_4^{2-} ions) and the indium concentration in the solution.

The cathode potential decreases with decreasing concentration, as can be seen from the dependence of the potential on the concentration:

$$E = E_0 + \frac{RT}{nF} \ln c,$$

where E_0 is the normal potential (i. e., potential at the ionic concentration

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of 1 N), c is the ion concentration in the solution, n is the valency of the ion, and F is the Faraday number.

This causes a decrease in the difference between the absolute values of the potentials of the metal to be deposited by cementation and the metal on which cementation takes place and leads to a slow-down of the cementation process.

Increasing the concentration of excess sulfuric acid also causes a shift of the cathode potential of indium in the direction of more negative values. This is attributed to the binding of indium ions as complex salts, which reduces the concentration of indium ions in solution

$$In^{3+} + 2SO_4^{2-} \rightleftarrows [In(SO_4)_2]^-.$$

The cementation on aluminum is favored by the presence of chloride ions (10 to 20 ml of hydrochloric acid is added to one liter of the solution). This may probably be attributed to the partial decomposition of the sulfate complex in the presence of chloride ions:

$$[In(SO_4)_2]^- + 3Cl^- \rightleftarrows InCl_3 + 2SO_4^{2-}.$$

Moreover, the hydrochloric acid dissolves the passivating oxide layers formed on the aluminum surface.

The cementation of indium on aluminum yields a precipitate which can be readily removed from the surface, a fact which makes this process advantageous as compared with the cementation on zinc.

The presence of appreciable amounts of arsenic in the solution leads to incomplete precipitation of indium; this is attributed to the formation of indium orthoarsenite $InAsO_3$ which has a low degree of dissociation. Hence, in the case of solutions with a high arsenic concentration the arsenic must be separated from the solution (e.g., by cementation on iron in the presence of copper).

The indium sponge produced by the cementation is washed with water, pressed into pellets and fused under a protective layer of sodium hydroxide. The crude product contains 96 to 99% indium, depending on the impurity concentration in the starting solution.

Examples of technological processes for the production of crude indium

Usually, the production of crude indium from indium-containing products combines the above-described methods for the isolation of concentrates and the removal of impurities. A variant of the technological flow sheet for the processing of oxides prepared by distillation in a rotary kiln is shown in Figure 184.

The oxide containing ~ 0.03 to 0.07% indium is subjected to acid leaching. The insoluble lead sulfate remains in the residue (the lead cake). The indium-containing solution is separated by filtration and is neutralized with zinc oxide to pH 4.8 to 4.9. This yields a hydrated precipitate containing 0.1 to 0.2% indium. The precipitate is redissolved and iron turnings are added to the solution to cause partial precipitation of the copper and arsenic (by cementation). The solution is again neutralized with zinc oxide (the dissolution and neutralization stages are

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sometimes repeated two or three times). The hydrated precipitate is treated with an alkali solution with intensive heating. As a result of the alkaline treatment, sodium stannate, aluminate, and gallate pass into the solution while the indium remains in the precipitate since the sodium indates are unstable in a boiling solution.

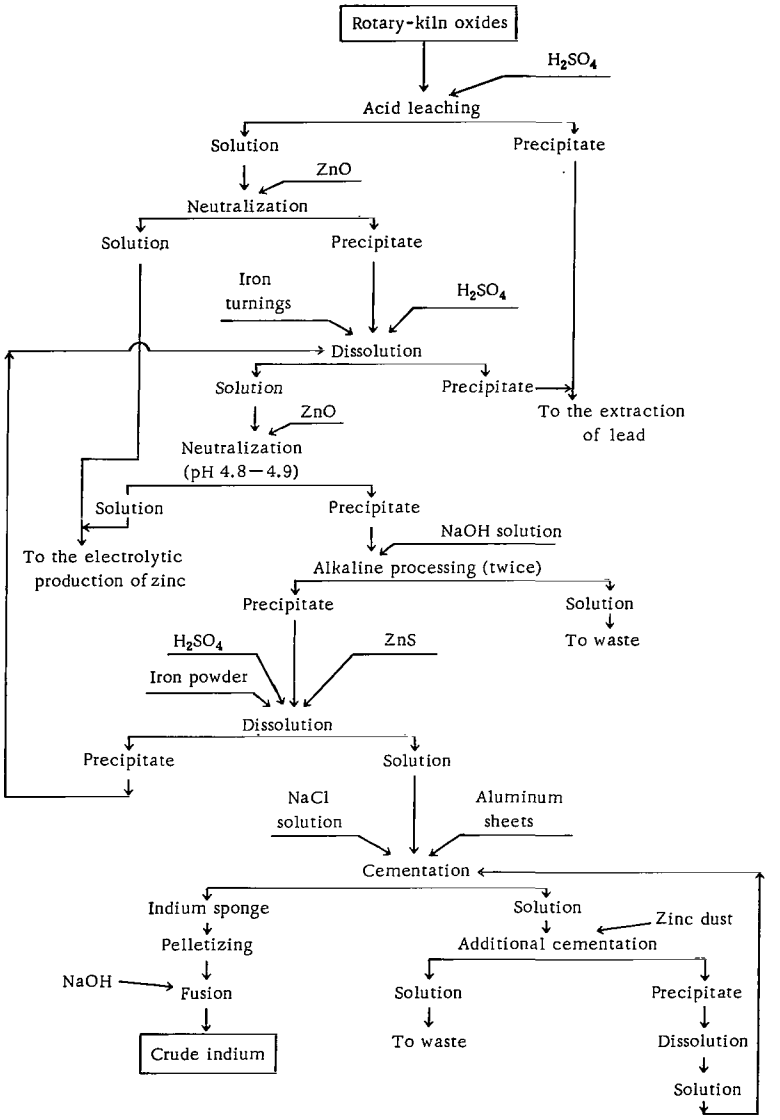

FIGURE 184. A typical flow sheet of the extraction of indium from the rotary-kiln oxides.

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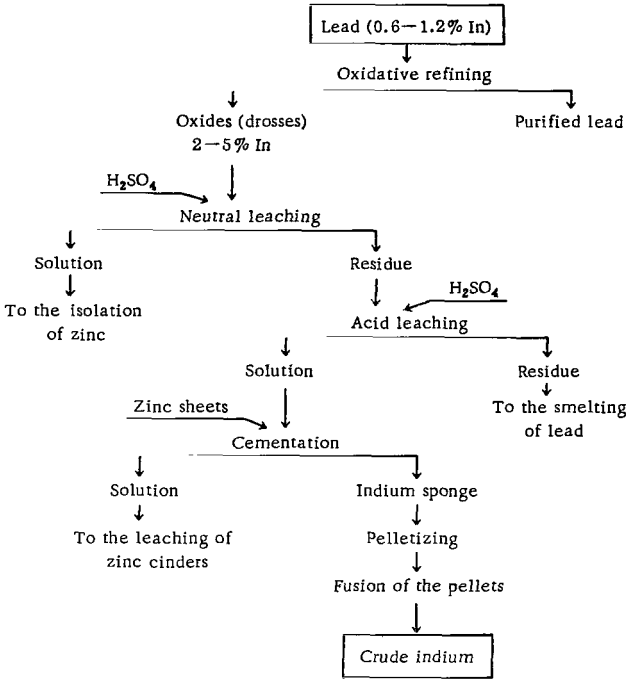

FIGURE 185. Extraction of indium from the lead produced in the refining of crude zinc.

The precipitate is dissolved in sulfuric acid and the copper and arsenic are removed from the solution by adding iron powder and zinc sulfide. The copper is cemented on the iron while the arsenic and other impurities (Pb, Bi) are precipitated as the sulfides. The indium is separated from the purified solution by cementation on aluminum sheets. This causes the precipitation of up to 95% of the indium. The indium remaining in the solution is subsequently precipitated on zinc dust, which is then dissolved in sulfuric acid and the solution is returned to the first cementation stage. The indium sponge produced is fused in steel crucibles under a layer of sodium hydroxide. The crude metal contains 98 to 99% indium.

As another example, we shall describe one of the methods of extracting indium from the lead produced in the refining of crude zinc (Figure 185). The lead, containing 0.6 to 1.2% indium, is taken for oxidative refining. The resulting oxides (drosses) contain 2 to 5% In, 15 to 16% Zn, 73 to 74% Pb, and some other elements. They are subjected first to neutral and then to acid leaching. The bulk of the lead remains in the solid residue. The indium is precipitated from the solution (which contains 10 g In/l) by cementation on zinc sheets. The crude metal obtained after fusion under a layer of sodium cyanide contains 94 to 96% In. The concentrations of the main contaminants are 0.3 to 1.5% Sn, 0.2 to 1.0% Tl, 0.2 to 1.5% Zn, $< 0.5\%$ Cd, and $< 3\%$ Pb.

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The total degree of extraction of the indium from the lead into the crude metal is about 90% /19/.

94. REFINING OF CRUDE INDIUM

The crude indium contains a number of impurities: Cd, Pb, Al, Zn, Sn, Cu, Fe, Tl, etc.

Since indium is used in semiconductor electronics, the refining is carried out with special care.

The following refining methods are used in practice:

1) selective cementation,
2) electrochemical methods,
3) chemical methods,
4) vacuum distillation,
5) zone melting and rod drawing from melt.

In actual practice, use is made of a combination of several of those methods.

Selective cementation

The crude indium is dissolved in sulfuric acid and some of the impurities are then separated by cementation, using the differences in the normal potentials of the elements (see p. 460). For instance, the tin present as an impurity is separated by cementation on crude indium plates. After prolonged contact (70 to 100 hours) between the solution of indium in sulfuric acid and the cementation-base metal, the tin concentration in the solution is reduced to 0.003 g/l.

It has been suggested that thallium and cadmium be removed from the solution by slow cementation on cast plates of zinc containing $\sim 1\%$ In and $\sim 0.3\%$ Cd. Cadmium and thallium are deposited on the zinc together with a very small fraction of the indium. The mechanism of this process has not been elucidated. In order to have a satisfactory deposition it is required that the zinc plates have a fresh active surface; hence, they are remelted every day. It must be noted that the above purification method is complicated and has been recently replaced by simpler methods.

Electrochemical methods /20, 24, 25/

Indium can be freed from many impurities by electrolytic refining in which the crude indium is used as a soluble anode. The nobler metals (Sn, Pb, Cu) remain in the anodic slimes while the metals less noble than indium (Al and other) remain in the solution.

Electrolytes of various compositions have been proposed for the electrolytic refining of indium. The baths most commonly used contain indium sulfate and sodium chloride. A sample bath composition is as follows: In (as the sulfate) 40 to 60 g/l, NaCl up to 100 g/l and animal glue 1.0 g/l at pH 2 to 2.5.

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The addition of glue makes it possible to obtain compact cathodic deposits. The crude indium anodes are enclosed in cotton bags in order to prevent the transfer of fine lead, tin, and copper particles to the cathode. The cathode may be made of high-purity indium or aluminum sheets. The electrolysis is carried out at a cathodic current density of about 100 amp/m2 and at a voltage of about 2 V.

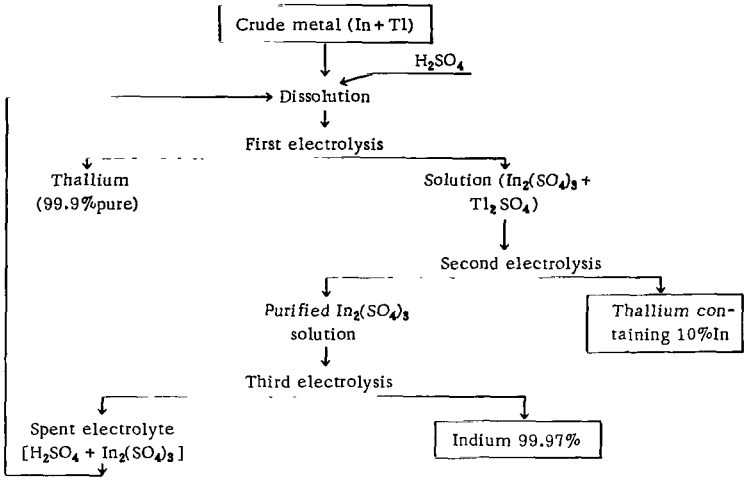

FIGURE 186. Flow sheet of the electrochemical separation of indium and thallium.

Indium of a degree of purity of 99.995 to 99.999% may be obtained by repeating the electrolytic refining twice.

If the crude indium contains thallium (which was not separated in the preceding purification stages), it may be separated in the electrolytic refining /25/ in spite of the fact that the potentials of the cathodic reactions In^{3+}/In and Tl^{+}/Tl are quite close. This is explained by the fact that indium is present in the solution as a trivalent ion whose reduction on the cathode comprises several stages. The last stage involves the reduction of monovalent indium to the metal. Thallium, which is present in the solution as a monovalent ion is oxidized at the anode to the trivalent state. Monovalent indium ions cannot exist in the presence of Tl^{3+} ions, since they are rapidly oxidized; this causes an interruption in the cathodic deposition of the indium*:

$$In^{+} + Tl^{3+} \rightarrow In^{3+} + Tl^{+}.$$

A vigorously stirred electrolyte always contains Tl^{3+} ions. Hence, thallium is deposited in the first stage of the electrolysis, but when its concentration in the electrolyte decreases it is deposited together with indium and finally, indium is deposited in a pure state.

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* The potential of the system Tl^{3+}/Tl^{+} is + 1.21 V while that of the system In^{3+}/In^{+} is -0.4 V.

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Eighty percent of the thallium (~99.9% pure) may be isolated in the first stage, while the remaining 20% is deposited in the second stage, contaminated with 10% In. Pure indium may be then deposited from the thallium-free solution (Figure 186).

Chemical methods

The fusion of indium sponge under a layer of alkali is extensively used. This method is used in the first stage of refining for the separation of the bulk of impurities — lead, zinc, tin, aluminum, and gallium — which dissolve in the molten alkali. The fusion is usually carried out in steel crucibles at 320 to 350°. A more thorough purification is accomplished by melting the indium at 250° under a molten 3 : 1 mixture of $ZnCl_2$ and NH_4Cl /26/. Thallium is the first to be dissolved by the molten salts, through the reaction:

$$NH_4Cl + Tl \rightarrow TlCl + NH_3 + {}^1/_2H_2.$$

When the slag (molten salt) is poured out, it contains all the thallium and a fraction of the indium. A second melting, under a fresh batch of the molten-salt mixture, extracts into the second slag most of the indium together with cadmium. The residual indium button contains Pb, Sn, Cu, and Ag contaminants. Pure indium is isolated from the second slag. The indium is present in the slag as the chloride of monovalent indium InCl. This is attributed to the following reactions:

$$In + 2NH_4Cl = InCl_2 + 2NH_3 + H_2;$$
$$In + ZnCl_2 = InCl_2 + Zn;$$
$$InCl_2 + In = 2InCl.$$

Thus, the indium is dissolved at first (by the molten salt) as the dichloride. The dichloride is then reduced by the molten indium to the monochloride InCl.

Pure indium is isolated from the slag and separated from the cadmium by the disproportionation method. The disproportionation of InCl from the slag is carried out in an aqueous solution, yielding indium and $InCl_3$ /26/:

$$3InCl \rightarrow 2In + InCl_3.$$

In theory, treating the slag with water should cause the precipitation of 2/3 (66.6%) of the indium. Actually, only 50% of the indium is precipitated since not all the indium in the slag is in the form of InCl. After its processing with water the pulp is acidified with hydrochloric acid to dissolve the zinc hydroxide which may be present in the oxide as a result of the partial hydrolysis of the zinc chloride.

Pure indium dissolves slowly in cold dilute hydrochloric acid and the losses of indium during the processing are negligible. The indium remaining in the aqueous solution may be isolated by electrolysis or cementation and returned for refining (if necessary). The residual alloy, with the impurities (Pb, Sn, Cu, and Ag) in it, is dissolved in hydrochloric or sulfuric acid, indium is precipitated from the solution and is returned to the purification cycle. A flow sheet of the process is shown in Figure 187.

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The impurity concentration in indium purified by the above method is $1 \cdot 10^{-4} - 3 \cdot 10^{-4}$%. This method is of great interest for the removal of thallium, cadmium, and some other impurities from the indium.

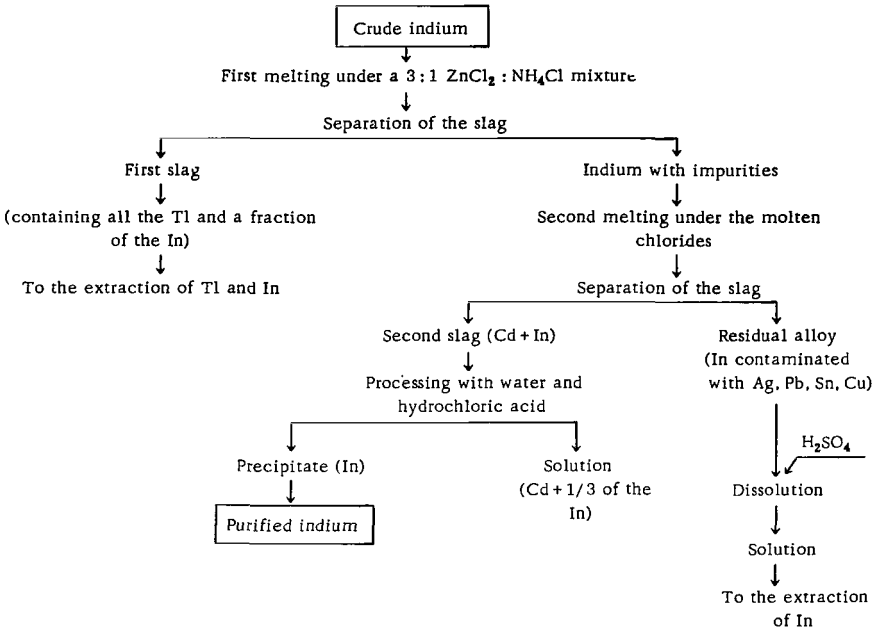

FIGURE 187. Flow sheet of the refining of indium by dissolution in molten salts and disproportionation.

Thorough purification of the indium (to remove the lead) may be accomplished by precipitation of lead sulfate from indium chloride solutions in the presence of a coprecipitant — barium sulfate /27/. For this purpose, sulfuric acid and barium chloride are added to the solution. During the formation of the almost insoluble $BaSO_4$ (its solubility product is $1.1 \cdot 10^{-10}$) the small amount of lead ions present in the solution is entrapped in the crystalline lattice of the barium sulfate and is coprecipitated with it. The lead concentration in indium purified by the above method does not exceed $2 \cdot 10^{-5}$%.

Vacuum distillation

This method may be used to free the indium from metals with a low boiling point. Thus, cadmium (bp 765°) may be separated by melting indium in a vacuum at 900°. The cadmium concentration in the indium may be reduced to 10^{-5}%.

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Zone melting and rod drawing from melt

These purification methods are used to produce the high-purity indium used in semiconductor electronics* /28/.

The indium is melted in boats (zone melting) or crucibles (the drawing method) made of pure quartz or pure dense graphite. The melting is carried out in vacuo or under a purified argon, nitrogen, or hydrogen atmosphere.

The USSR standards with respect to the impurity content of high-purity indium are as follows: Zn, Cd, Cu, Sn, As — not more than 0.0001% of each, Fe — maximum 0.001%, Pb — maximum 0.005%.

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* The nature of the zone melting and rod drawing from melt methods has been described in the chapter on germanium.

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Chapter X

THALLIUM

95. GENERAL DATA ON THALLIUM

Properties of thallium

The element thallium was discovered in 1861 by Crookes by a spectroscopic method, in the sludge from the production of sulfuric acid by the chamber process. Its presence was indicated by a characteristic green line in the spectrum.

Thallium is a soft silvery-white metal. It tarnishes rapidly in the air at room temperature through the formation of a black film of thallous oxide Tl_2O which slows down further oxidation of the metal. The metal is rapidly oxidized above 100° with the formation of a mixture of oxides (Tl_2O and Tl_2O_3).

From the standpoint of its mechanical and some physical properties thallium resembles lead (Table 61).

Thallium is slowly corroded by water in the presence of air. The metal is rapidly dissolved by nitric acid and more slowly by sulfuric acid. Thallium is sparingly soluble in hydrochloric acid, because of the formation of a film of the sparingly soluble thallium chloride. It is insoluble in alkali solutions. It reacts with chlorine, bromine, and iodine at room temperature, and with sulfur on heating.

The properties of thallium compounds

Thallium belongs to Group III of the periodic table. In spite of being an analogue of gallium and indium, thallium differs sharply from these elements in its chemical properties.

The peculiarity of thallium is associated with the fact that the compounds of monovalent thallium are more stable than those of trivalent thallium. In some properties the monovalent thallium compounds resemble the compounds of the alkali metals and silver. The similarity with the alkali metals is exhibited in the formation of readily soluble monovalent thallium hydroxide Tl(OH) which is a strong base, in the formation of soluble carbonate, sulfate, and ferrocyanide, and in the formation of double sulfates of the alum type and of a chloroplatinate $Tl_2(PtCl_6)$.

Like silver, monovalent thallium forms sparingly soluble halides (the solubility decreases in the order TlCl — TlBr — TlI), chromates, and sulfides. Unlike the silver ion, monovalent thallium does not form ammoniacal complexes.

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TABLE 61

Physical constants of thallium and lead

Constant	Thallium	Lead
Atomic number	81	82
Atomic weight	204.39	207.22
Density	11.85	11.34
Crystalline lattice	α-thallium hexagonal stable up to 230°; a = 3.450 Å, c = 5.520 Å; β-thallium face-centered cubic, stable above 230°; a = 4.841 Å	Face-centered cubic, a = 4.9396 Å
Melting point, °C	303	327.4
Boiling point, °C	1460	1740
Brinell hardness, kg/mm²	3	5
Tensile strength, kg/mm²	0.9	1.9
Specific heat, cal/g °C (at 20—100°)	0.0326	0.031
Heat conductivity, cal/cm·sec, °C	0.093	0.083
Linear expansion coefficient	$28 \cdot 10^{-6}$	$29.3 \cdot 10^{-6}$
Volume expansion upon solidification	3.23	—
Electrical resistivity at 20°, ohm·cm	$18 \cdot 10^{-6}$	$20.38 \cdot 10^{-6}$
Transition temperature to the superconducting state, °C	2.38	—
Thermal neutron capture cross section, barns	3.3	0.2

Monovalent thallium is oxidized to the trivalent state by using strong oxidizing agents such as potassium permanganate, chlorine, and aqua regia.

Thallium compounds are poisonous and their effect is similar to that of arsenic.

Thallium forms two oxides: the brown thallic oxide Tl_2O_3 and the black thallous oxide Tl_2O. Tl_2O_3 is formed upon the oxidation of thallium in ozone. Noticeable dissociation of Tl_2O_3 takes place above 100° with the formation of Tl_2O:

$$Tl_2O_3 \rightarrow Tl_2O + O_2.$$

Complete decomposition occurs at 700 to 750°. The heat of formation of Tl_2O_3 is 120 kcal/mole, that of Tl_2O is 43 kcal/mole.

Thallous oxide is a hygroscopic powder melting at about 300°. It dissolves in water yielding the hydrate TlOH. The solubility of TlOH in water at 0 and 100° is 20 and 59.7% respectively.

Thallium hydroxide $Tl(OH)_3$ separates out as a brown precipitate upon the addition of alkali to a solution of a trivalent thallium salt. In dilute solutions the precipitation of $Tl(OH)_3$ starts at pH $\approx$ 3.0 to 4.0. The heat of formation of $Tl(OH)_3$ is 122.6 kcal/mole, the solubility product is $\sim 10^{-16}$.

The properties of some thallium salts are listed in Table 62.

With the exception of thallium fluoride, thallium halides are sparingly soluble in water. Thallium chloride, bromide, and iodide are sensitive to light and decompose under illumination. Thallium sulfate is isomorphous with the sulfates of potassium, rubidium, and cesium; it forms double salts with the sulfates of trivalent metals, e.g., $TlAl(SO_4)_2 \cdot 12H_2O$.

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Thallium carbonate Tl_2CO_3 is hydrolyzed in solution.

In a neutral medium or an acetic acid solution thallium is quantitatively precipitated (as the sulfide) by ammonium sulfide or hydrogen sulfide. The sulfide dissolves in inorganic acids.

TABLE 62

Properties of some salts of monovalent thallium

Property	TlF	TlCl	TlBr	TlI	Tl_2SO_4	Tl_2CO_3	Tl_2S	Tl_2CrO_4
Color	Colorless		Yellowish	Yellow	Colorless		Black	Yellow
Density, g/cm^3	—	7.0	7.5	7.07	—	—	—	—
Melting point, °C	327	429	460	440	—	—	—	—
Boiling point, °C	655	806	819	823	—	—	—	—
Solubility in water (%) at:								
0	—	0.17	0.0024	0.0024	2.7	2.75	From 0.0015 to 0.01	0.03
20	45	0.32	0.0476	0.0063	4.86	5.50		—
40	—	0.60	0.104	—	7.59	8.1		—
60	—	0.01	0.004	—	10.9	13.0		—
100	—	2.32	—	—	—	25.9		0.20
Heat of formation, kcal/mole	77	49	42	31	—	—	20.8	—

Thallium chromate Tl_2CrO_4 is precipitated from weakly alkaline and neutral solutions upon the addition of potassium or sodium chromate. The yellow thallium bichromate $Tl_2Cr_2O_7$, or a mixture of the bichromate and the chromate is precipitated from acid solutions. Thallium bichromate is sparingly soluble in cold nitric and sulfuric acids.

Uses of thallium /3, 33/

Thallium and its compounds are used in various branches of technology. Of greatest interest are the uses of thallium in semiconductor electronics, instrumentation and infrared optics.

Thallium sulfide and oxysulfide are used for the production of photocells which are highly sensitive to infrared light. These photocells are used as signaling devices in darkness or in a dense fog. Thallium sulfide photoelements are of special importance for aviation. They are used for the production of infrared projectors indicating the landing strips in darkened airfields and in infrared photography.

Thallium is used in the production of selenium rectifiers. A selenium rectifier consists of a layer of selenium deposited upon a nickel-plated iron plate. A layer of a cadmium-tin-bismuth alloy (serving as the upper electrode) is applied over the selenium layer. The introduction of thallium into the composition of the upper electrode increases the back voltage of the rectifier to 40 V (as compared with 30 V in conventional rectifiers).

Thallium bromide or iodide serve as the activators in phosphors (luminescent substances — alkali metal halide crystals) used in scintillation counters for β-particles or γ-rays.

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A radioactive isotope Tl^{240} (half-life = 2.7 years) is used as a β-radiation source in material-testing instruments (defectoscopes) and in process control, in particular for the measurement of the thickness of products and coatings.

A thallium gas-discharge tube (i.e., a glass tube filled with argon and thallium vapor) emits monochromatic light with a wavelength of 5350 Å (green). This tube is used for the calibration of spectroscopic instruments, for the control of photographic paper and films, and for the evaluation of X-ray pictures in medicine.

Monocrystals of a solid solution of thallium bromide and iodine (about 42% TlBr and 58% TlI) are used for the production of windows, lenses, prisms, and cells for optical instruments operating in the infrared region of the spectrum. They are used in infrared military devices and in spectroscopes and microscope objectives for work in the infrared region of the spectrum.

The addition of thallium carbonate to the initial materials in glass manufacturing imparts to the glass a high refractive power.

Thallium is a component of a number of bearing alloys to which it imparts a high anti-friction coefficient. Thus, the alloy containing 72% Pb, 15% Sb, 5% Sn, and 8% Tl is superior to the best tin-based bearing alloys.

The introduction of thallium to lead alloys improves their corrosion resistance. For instance, the alloy containing 70% Pb, 20% Sn, and 10% Tl is not attacked by hydrochloric and nitric acids. This and some other lead-thallium alloys may be used as insoluble anodes in the electrodeposition of metals.

Thallium sulfate was used in agriculture as a poison (against rodents), but has been displaced by cheaper poisons.

Thallium salts may be used as anti-knock additives to fuels for internal combustion engines, as catalysts for organic synthesis, etc.

96. OCCURRENCE

The thallium concentration in the Earth' s crust is $3 \cdot 10^{-4}$% by weight. Some thallium minerals are known to exist, but most of the thallium is scattered in the form of an isomorphous contaminant in the sulfide minerals of lead, zinc, iron, and copper, and in silicates (felspar, micas, lepidolite) in which it replaces potassium and rubidium. The highest concentrations of thallium are encountered in iron sulfides (pyrites and marcasite). The thallium concentration in these minerals reaches 0.1 to 0.5% /32/. At present, most of the thallium is extracted from the wastes and intermediate products obtained in the processing of sulfide ores.

During the oxidizing and agglomeration roasting of sulfide concentrates, a fraction of the thallium is entrained with the gases and concentrates in the dust collected in the electrostatic filters and other dust-trapping devices. This is attributed to the volatility of thallium oxide Tl_2O and thallium chloride (which is formed upon the addition of chlorides during the agglomeration of the charge) at the roasting temperature (800 to 1000°).

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The vapor pressure of Tl_2O at 900° is 120 mm Hg, while the vapor pressure of TlCl reaches 1 atm at 806°. In the agglomeration roasting of lead concentrates more than 50% of the thallium is entrained with the gases. The dust from the electrostatic filters usually contains a few tenths of one percent of thallium /35/.

In the shaft furnace smelting of lead, also, a fraction of the thallium is entrained with the gases and concentrates in the dust.

In the roasting of zinc concentrates a fraction of the thallium concentrates in the dust together with the cadmium. The thallium remaining in the cinders is dissolved during the leaching. When the cadmium and copper are removed from the solution by cementation on zinc dust, the thallium passes into the copper-cadmium cake.

The dusts from the processing of copper concentrates in roasting and smelting furnaces are enriched with thallium.

Thallium may also be produced from the dusts collected in the installation for the purification of the roasting gases in sulfuric acid plants.

Thallium may thus be extracted from the dusts of lead, zinc, copper, and sulfuric acid manufacturing and from the copper-cadmium cake produced in the hydrometallurgical processing of zinc cinders.

97. EXTRACTION OF THALLIUM FROM INDUSTRIAL WASTES

The industrial products enriched in thallium usually contain a few tenths of one percent of thallium. Thallium concentrates are produced by pyrometallurgical and hydrometallurgical methods.

Pyrometallurgical production of thallium

The pyrometallurgical enrichment methods are based on the volatility of the thallium compounds, Tl_2O and TlCl. When a mixture of a thallium-containing material and coal is roasted in rotary furnaces at 1100 to 1200° (as in the rotary-kiln process) most of the thallium is volatilized as Tl_2O.

An effective method for the concentration of thallium is based on chlorination roasting with common salt, which leads to the volatilization of thallium chloride. The roasting is carried out at 800 to 900°. The main reaction involved is:

$$Tl_2O + 2NaCl + SO_2 + {}^1/_2O_2 = 2TlCl + Na_2SO_4.$$

The sulfur dioxide needed for the reaction is formed through the oxidation of the sulfides and through the thermal decomposition of the copper and iron sulfates.

Hydrometallurgical production of thallium

The hydrometallurgical methods involve the leaching of the material and the separation of thallium-enriched precipitates from the leach liquors.

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If the materials to be processed have been produced by cementation (e.g., copper-cadmium cakes), and in which the components are in a metallic form, the materials are subjected to preliminary oxidative roasting in order to facilitate the leaching.

The thallium in the dusts is mainly in the form of Tl_2O and thallium chloride.

The leaching may be carried out either with water (thallous oxide is readily soluble in water) or with dilute sulfuric acid.

Thallium is separated from the solution as the hydroxide, chloride or chromate, or by cementation. The selection of the method to be used depends on the thallium concentration in the solution and on the concentrations of other elements accompanying the thallium.

Precipitation of thallium hydroxide. This method is used for the isolation of thallium from dilute solutions (0.05 to 1 g Tl/l). Thallium hydroxide $Tl(OH)_3$ is precipitated at pH $\cong$ 4, which makes it possible to separate the thallium from the bulk of the cadmium and zinc ($Cd(OH)_2$ is precipitated at pH $\cong$ 8, while $Zn(OH)_2$ is precipitated at pH $\geqslant$ 5.2). The thallium in the leach liquors is present as the monovalent ion. The Tl^+ is oxidized to Tl^{3+} by means of potassium permanganate or ammonium persulfate. The oxidation with potassium permanganate involves the reaction:

$$3Tl_2SO_4 + 4KMnO_4 + 8H_2SO_4 = 3Tl_2(SO_4)_3 + 4MnO_2 + 2K_2SO_4 + 8H_2O,$$

whose main product is tetravalent manganese since the Mn^{2+} ions are oxidized by excess permanganate to MnO_2.

After the oxidation the solution is neutralized with sodium hydroxide to pH 4 to 5, and heated to 70 to 80° with hydrolysis of the thallium sulfate:

$$Tl_2(SO_4)_3 + 6H_2O \rightarrow Tl(OH)_3 + 3H_2SO_4.$$

The hydrated manganese dioxide formed during the oxidation sorbs the thallium hydroxide and thus facilitates the more quantitative precipitation of the thallium.

Precipitation of thallium chloride. The precipitation of the sparingly soluble chloride is used in several technological processes. This method should be employed for solutions with relatively high thallium concentrations (above 5 g/l).

The solubility of TlCl in water at 20° is about 0.32% (see Table 63). The presence of an excess of the precipitating agent (usually NaCl) reduces the solubility and thus leads to a fairly quantitative precipitation. The effect of the NaCl concentration on the solubility of the TlCl is as follows:

NaCl concentration, %	0	0.146	0.293	0.858	1.17
TlCl solubility, %	0.32	0.208	0.142	0.095	0.065.

It should be mentioned that the precipitated thallium chloride usually contains a considerable amount of cadmium which is coprecipitated with the thallium as the double chloride $TlCl \cdot CdCl_2$. In order to reduce the cadmium content of the precipitate, the precipitation should be carried out at as low a temperature as possible.

Precipitation of thallium chromate. Thallium may be precipitated from weakly acid solutions as the yellow sparingly soluble bichromate $Tl_2Cr_2O_7$. Sodium bichromate is used as the preciptating agent.

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This method is used primarily in the case of solutions with a high thallium content. When thallium bichromate is precipitated from solutions of a low thallium content (0.5 to 1 g Tl/l) the precipitation is not quantitative.

The thallium bichromate precipitates containing 20 to 30% Tl are decomposed with sulfuric acid in the presence of a reducing agent (zinc or hydrogen sulfide) which is added in order to reduce the hexavalent chromium to the trivalent state.

Cementation of thallium on zinc or zinc amalgam /34/. The isolation of thallium by cementation on zinc is extensively used in manufacturing practice. The cementation is usually carried out from weakly acid solutions, on zinc sheets from which the thallium is easily removed.

A method for the cementation of thallium on zinc amalgam, which makes it possible to extract up to 98% of the thallium even from dilute solutions (0.1 to 0.2 g Tl/l), was developed recently in the USSR. The cementation of thallium on zinc amalgam is based on the substitution reaction:

$$Zn/Hg + 2Tl^{+} \rightleftarrows 2Tl/Hg + Zn^{2+}.$$

Cadmium, lead, copper, and tin may undergo cementation together with the thallium. Iron, nickel, and cobalt remain in the solution (contrary to the case of cementation on zinc) since the cathodic deposition potentials of these elements on zinc amalgam are shifted to the side of negative values more strongly than in the case of thallium:

	Co/Co^{2+}	Ni/Ni^{2+}	Fe/Fe^{2+}	Tl/Tl^{+}
Normal deposition potential, V	-0.277	-0.25	-0.44	-0.336
Deposition potential on zinc amalgam, V	-0.98	-0.83	-0.96	-0.58

The thallium amalgam formed is then subjected to electrolysis and the thallium is deposited on the cathode. This is accompanied by further purification of the thallium.

Examples of technological processes

Various combinations of the above methods of separation of thallium from the solution are used in manufacturing practice. As illustrative examples, we shall describe below three processes for the extraction of thallium from the dusts of lead plants.

A **technological process involving the precipitation of** $Tl(OH)_3$ (Figure 188). The dust containing 0.04 to 0.12% Tl is leached with dilute H_2SO_4 (the final pH of the solution is about 2). The leaching is carried for $\sim$ 10 hours at 80° at a solid : liquid ratio of 1 : 5. The leach liquor extracts up to 90% of the Tl. The thallium concentration in the solution is 0.06 to 0.15 g/l. The thallium is then precipitated as $Tl(OH)_3$.

The Tl^{+} is oxidized at the beginning by the addition of permanganate to the solution (about 3 to 4 g/l), the solution is then neutralized with alkali to pH $\approx$ 4.5 to 5 and heated to 70°. After separation (by filtration) and drying the hydroxides, the precipitate has the following approximate

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composition: 0.4 to 0.6% Tl, 20 to 25% As, ~ 20% Mn, 0.9 to 1.4% Cd, 6 to 14% Zn, 0.02 to 0.06% Cu, 4.5 to 8% Fe.

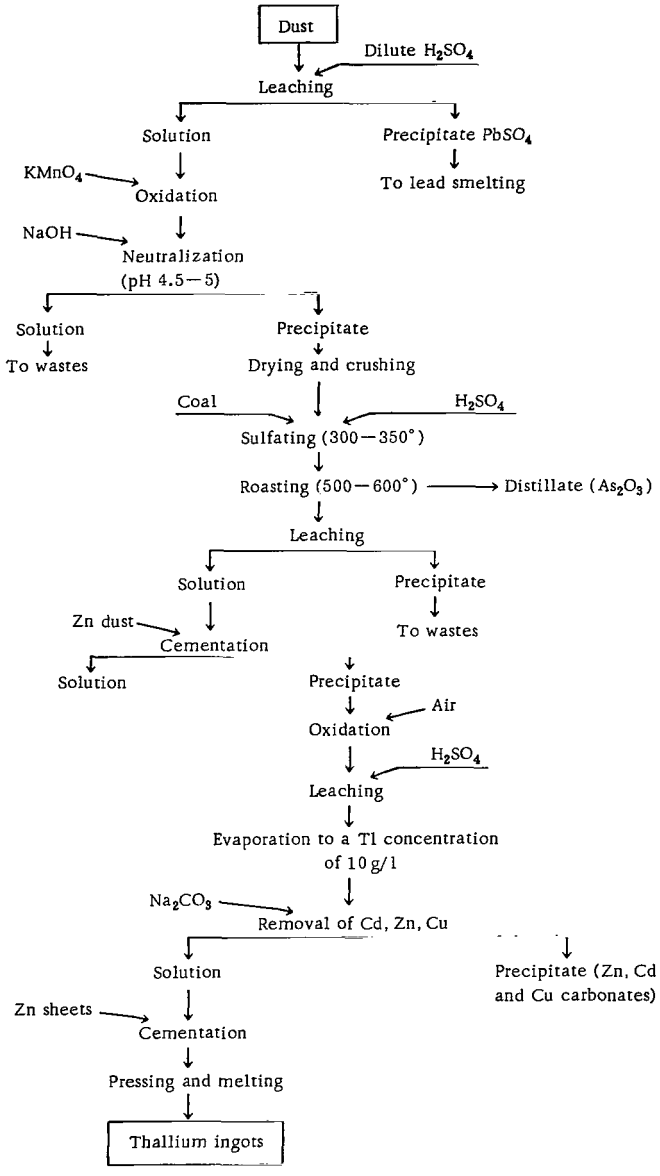

FIGURE 188. Flow sheet for the extraction of thallium from dust, including a $Tl(OH)_3$ precipitation stage.

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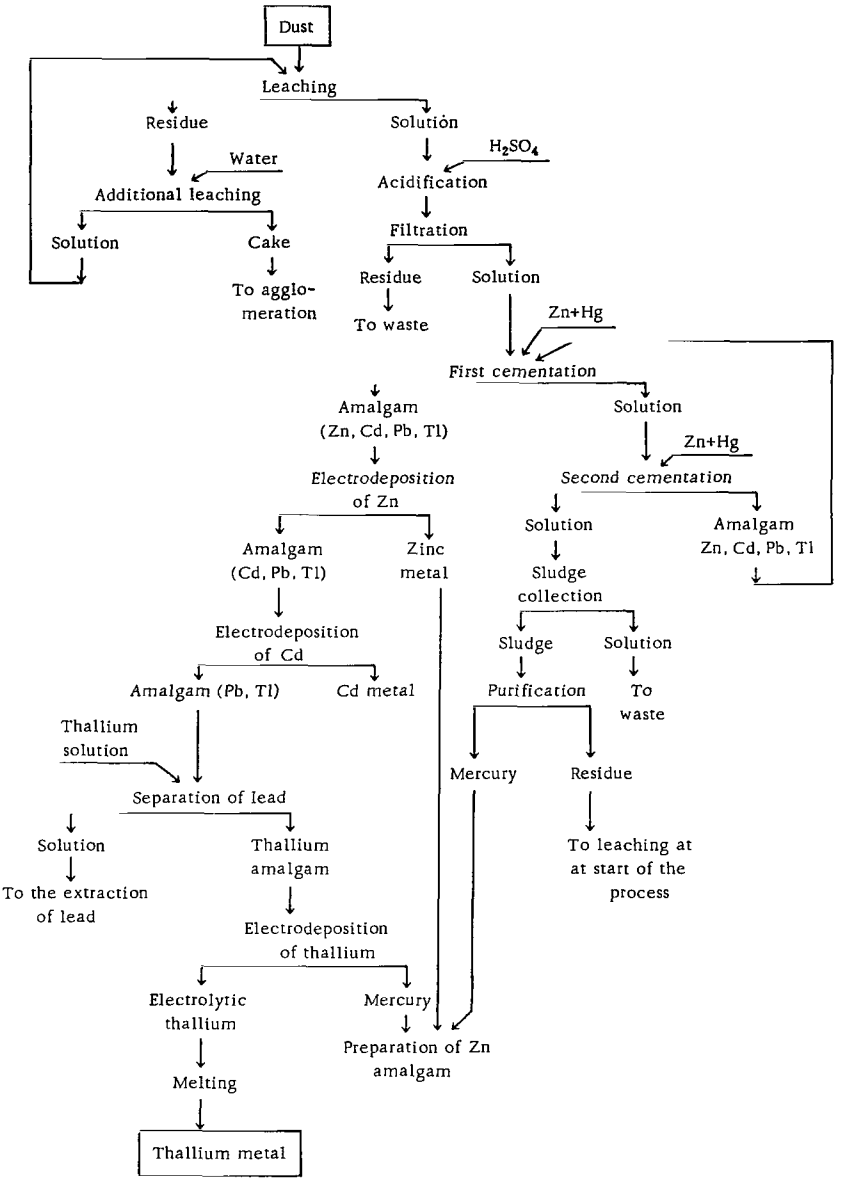

FIGURE 189. Flow sheet of the production of thallium from lead plant dusts by the amalgam method.

In order to separate the arsenic, the dried precipitate is mixed with 60% H_2SO_4 and 2 to 4% coal, the mixture is transferred to iron trays and heated in a muffle furnace first to 300 to 350° (the sulfation stage) and then to 500 to 600°. Under such conditions most of the arsenic is

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volatilized as As_2O_3. The sulfatized material is leached with water at a solid : liquid ratio of 1 : 10 at 80°. The thallium is separated from the filtered solution by cementation on zinc powder. The cementation is carried out at pH ≈ 2, at 40°. This causes precipitation of up to 99.5% of the thallium; the cementation precipitate contains 4 to 6% Tl. It is regarded as a thallium concentrate. In order to facilitate its dissolution, the precipitate is preliminarily oxidized in a stream of air at 200°. The oxidized material is leached with water, with heating. The solution is evaporated to a thallium concentration of about 10 g/l, and the copper, zinc, and cadmium present in the solution as contaminants are precipitated as the carbonates upon the addition of sodium carbonate. The thallium is then separated from the purified solution by precipitation on zinc plates (at pH 1). The thallium sponge formed is pressed into pellets and fused under a layer of sodium hydroxide. The metal produced in the above process contains about 96% thallium.

The amalgam method for the extraction of thallium (Figure 189) was developed in the USSR and is used for the extraction of thallium from the agglomerated dusts of a lead plant /34/. The dusts taken for processing contain 0.2 to 1.5% Tl.

The dust is leached with water in three stages at a solid : liquid ratio of 1 : 5 at 80 to 90°. The leaching is carried out in rubber-lined steel reactors fitted with stirrers (the rubber lining is necessary in order to prevent cementation of the thallium on the iron). The solution from the first leaching stage is taken for cementation while the solutions from the second and third leachings are returned to the preceding leaching stage. The extraction of thallium into the solution is 72 to 79%.

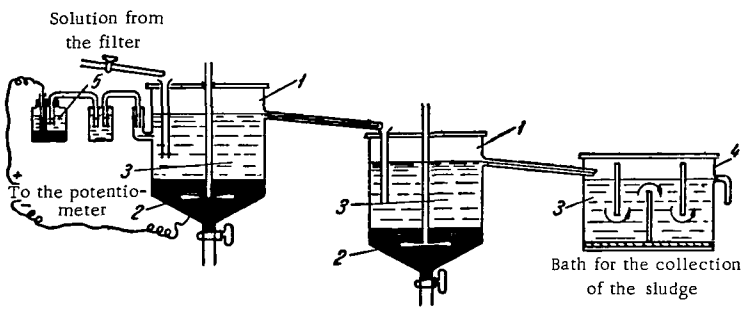

FIGURE 190. Diagram of a setup for the cementation of thallium on zinc amalgam.

1—reactors with stirrers; 2—amalgam; 3—solution; 4—collectors for the sludge; 5—cell for potential measurements.

The solution is acidified by the addition of H_2SO_4 (to 5 g/l) in order to obtain partial removal of the lead. The thallium is then separated in two stages by cementation on zinc amalgam. A diagram of the cementation set-up is given in Figure 190. The solution passes successively through two cementation reactors made of a vinyl polymer. Each of these reactors is charged with a known amount of mercury and zinc, producing an amalgam. The amount of zinc added to the first reactor is smaller and to the second reactor larger than the stoichiometric amount required for the quantitative cementation of the thallium. The consumption of zinc is easily

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controlled by measuring the amalgam potential. When all the zinc has been consumed, the amalgam potential drops sharply to 0.66 to 0.68 V (the potential of the zinc amalgam is 1.0 to 1.04 V)*. Zinc is added to the reactor to replace the zinc which has been consumed. After passing through the two reactors the solution is forwarded to a bath for the separation of the sludge (entrained mercury particles) and is collected in a receiver. The total degree of extraction of thallium into the amalgam is 93 to 98%. The bulk of the cadmium and lead from the solution are precipitated together with the thallium during the cementation.

In order to separate the metals composing the amalgam, it is electrolytically decomposed in three stages. Each stage is carried out in an electrolyte of a certain composition. The first stage involves the separation of the zinc. The electrolyte is a 2 N solution of $(NH_4)_2SO_4$ in 1 N NH_4OH. The second stage involves the separation of the cadmium. It is carried out in the same electrolyte. The third stage consists in the separation of the thallium. The electrolyte used is a 2 N solution of H_2SO_4.

The lead is separated by making use of the ability of thallium to displace lead from the amalgam. For this purpose the amalgam (after the electrodeposition of the cadmium) is treated with an alkaline solution containing thallium.

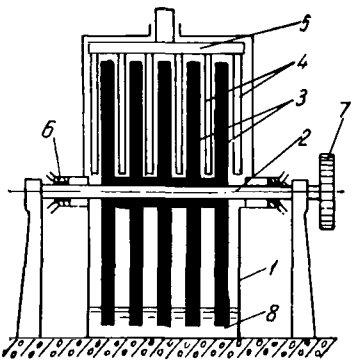

FIGURE 191. Diagram of an electrolyzer for the decomposition of the amalgam.

1—bath made of a vinyl polymer; 2—shaft; 3—copper discs—anodes; 4—aluminum plates—cathodes; 5—copper bus bar connected to the cathodes; 6—sealing; 7—pulley; 8—amalgam.

The amalgam is decomposed in electrolyzers made of a vinyl polymer (Figure 191). Five rotating copper discs immersed in the amalgam serve as the anodes. Their surface is rapidly coated with a layer of amalgam. The discs rotate at about 30 rpm. Aluminum plates, which are placed in the upper part of the bath in gaps between the discs, serve as the cathodes.

Zinc is deposited at an amalgam potential between -0.85 and -0.74 V, cadmium is deposited between -0.56 and -0.40 V, and thallium between -0.22 and -0.013 V (all the potentials given are with respect to the hydrogen electrode).

The thallium is deposited on the cathode as a sponge which is easily removed. The sponge is washed, pressed, and remelted.

Technological process involving a chloride precipitation stage /36, 37/ (Figure 192). The agglomeration dust containing 0.15% Tl is leached with hot water. The leach liquor contains 100 to 120 mg Tl/l. The degree of extraction of the thallium into the solution is 65 to 75%.

The thallium is precipitated from the solution with sodium sulfide. Cadmium, arsenic, antimony, and other elements are coprecipitated with the thallium as the sulfides. When the sulfide precipitate is dissolved in H_2SO_4 (at a solid : liquid ratio of 1 : 1 at 80 to 90°) the bulk of the impurities remains in the insoluble residue. Thallium is precipitated from the solution as thallium chloride upon the addition of common salt. The

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* These values of the potential are with respect to the normal calomel electrode.

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thallium chloride is decomposed with concentrated H_2SO_4 at 350 to 400°. The sulfate product is dissolved in water. At the same time soda ash is added in order to remove the cadmium from the solution. Thallium is separated from the solution by cementation on zinc sheets. The thallium sponge is pelletized and fused under a layer of sodium hydroxide.

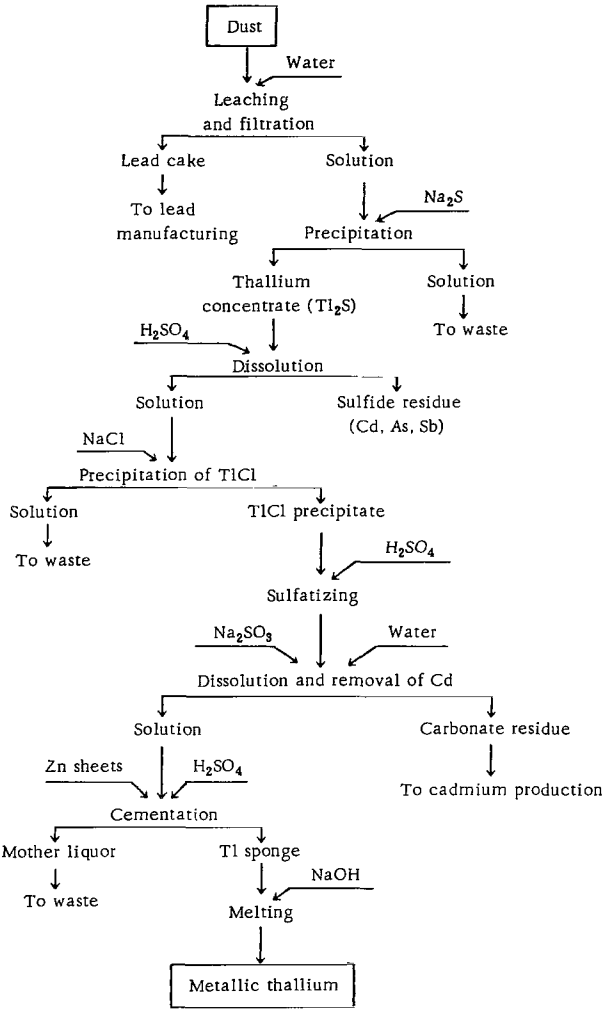

FIGURE 192. Flow sheet of the extraction of thallium from the agglomeration dust of a lead plant, including a chloride precipitation stage.

The thallium metal produced by the above method has an impurity content of a few thousandths of one percent. The degree of extraction of the thallium from the sulfide concentrate into the metal is 90 to 95%.

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98. PRODUCTION OF PURE THALLIUM

The technical specifications for thallium metal used in the manufacturing of bearing alloys and thallium salts for the optical industry are listed below:

Impurity	Pb	Cu	Cd	Zn	Fe
Permissible concentration,%	0.01	0.03	0.003	0.003	0.001.

The thallium content must be not lower than 99.96%.

The specifications with respect to the purity of the metal and its compounds are more rigorous. The strictest specifications are made in the case of thallium for use in semiconductor technology. The impurity content must not exceed $1 \cdot 10^{-5}$ to $1 \cdot 10^{-6}$%.

The thallium purification process includes alkaline refining of the metal with the addition of an oxidizing agent, electrolysis with a soluble anode, and zone melting or drawing from the melt.

Thallium does not react with molten alkalies. The impurities which are soluble in alkalies (lead, zinc, etc.) pass during the fusion of the thallium into the alkali melt. The alkaline refining is especially effective in the presence of oxidizing agents (KNO_3 or $NaNO_3$). However, in such a case up to 7% of Tl is dissolved by the molten alkali, the metal must be leached from the alkali melt and precipitated from the leach liquor as $Tl(OH)_3$. The consumption of alkali is about 10% (by weight) of the thallium pellets, the consumption of nitrate is 1 to 2%. The refining is carried out at 350°. After the alkaline refining the thallium is taken for electrolysis with a soluble anode. Zone melting is the last operation.

Thallium of a purity of 99.9995% is obtained from the metal containing 99.98% Tl by a combination of electrolytic refining and zone melting.

In the anodic dissolution of thallium in sulfuric acid (using nickel as the cathode) the silver, copper, and lead remain in the sludge. Thallium is then deposited on the cathode from the solution containing 18 g/l thallium and 70 g/l H_2SO_4, at 18° and a current density of 80 amp/m^2. The electrodeposited metal is purified by zone melting. The zone melting is carried out in an atmosphere of pure nitrogen, in quartz boats.

Thallium may also be purified by rod drawing from the melt, in a vacuum furnace at 300 to 305° (at a residual pressure of $5 \cdot 10^{-4}$ mm Hg), as described in the chapter on germanium /38/.

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Chapter XI

RHENIUM

99. GENERAL DATA ON RHENIUM

Brief historical note /1, 3/

In 1869 Mendeleev predicted the existence of two elements in Group VII which would the analogues of manganese and which were named by him "eka-manganese" and "dvi-manganese". They correspond to two elements which are known at present as technetium (atomic number 43) and rhenium (atomic number 75). During the 53 years following Mendeleev's prediction the discovery of the manganese analogues was reported by many investigators but has not been confirmed. It is now known that the search for element 43 in natural substances could not be successful since the element is unstable. This element was synthesized only in 1937 by Segre and Perrier by bombarding molybdenum nuclei with deuterons; it was named technetium (from the Greek word techne — artificial) to denote the fact that it was the first element to be prepared by artificial means.

In 1922 the German chemists W. and I. Noddack started a systematic search for manganese analogues in various minerals. By processing one kg of columbite they isolated 0.2 g of a product enriched with molybdenum, tungsten, ruthenium, and osmium. This product was found to contain a new element with the atomic number of 75, as confirmed by the characteristic X-ray spectrum. The Noddacks reported their discovery in 1925. They gave the name rhenium to the new element. A few months afterwards the Czech chemists Druce and Loring, as well as Heyrovsky and Dolejsek, reported that they had found element 75 in pyrolusite. It was subsequently found that the highest concentrations of rhenium occur in molybdenites.

Properties of rhenium /3, 5, 6/

Rhenium is a heavy refractory metal whose appearance resembles that of steel. Some of its physical properties are listed below.

Atomic number	75
Atomic weight	186.31
Lattice type and parameter	Close-packed hexagonal, $a = 2.76$ Å, $c = 4.45$ Å
Density, g/cm^3	21.0
Melting point, °C	3180 ± 20
Boiling point, °C	~ 5900
Vapor pressure (at 2225°), mm Hg	$1.18 \cdot 10^{-6}$
Heat capacity (average between 0—1200°), kcal/g, °C	0.03653

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Linear expansion coefficient:	
along the *C* axis	$12.45 \cdot 10^{-5}$
perpendicular to the *C* axis	$4.67 \cdot 10^{-6}$
Specific electrical resistance (ohm · cm · 10^6) at:	
20°C	19.8
2220°C	125
2710°C	134
Transition temperature to the superconducting state, °K	1.7
Electron work function, eV	4.8
Heat conductivity, cal/cm · sec, °C	0.17
Brinell hardness of the annealed metal, kg/mm²	200
Tensile strength of forged and annealed rods, kg/mm²	115.5
Modulus of elasticity, kg/mm²	47000
Thermal neutron capture cross section, barns	85

Rhenium has the second highest melting point of all metals (after tungsten); and the fourth highest density after osmium, iridium, and platinum. The specific electrical resistance of rhenium is almost four times that of tungsten and molybdenum.

In contrast to tungsten, rhenium is ductile in the cast and recrystallized states and may be subjected to cold deformation. Rhenium has a very high modulus of elasticity. Its hardness increases sharply after a small deformation (i.e., it is subject to pronounced work hardening), but returns to the ductile state after annealing in a protective atmosphere (hydrogen) or in vacuum.

In contrast to tungsten products, rhenium products withstand many heating-cooling cycles without losing their strength. Welded joints are not brittle. At temperatures up to 1200° rhenium is stronger than tungsten, and much stronger than molybdenum (Figure 193).

Rhenium is stable in air at room temperature. Oxidation of the solid metal, with the formation of rhenium anhydride Re_2O_7 starts above 300° and becomes rapid above 600°. Fine rhenium powder becomes moist upon storing in air, which is attributed to the oxidation to Re_2O_7, which absorbs moisture.

Rhenium does not react with hydrogen up to its melting point. As compared with tungsten, rhenium is much stabler in argon or in vacuum in the presence of moisture at high temperatures. The metal does not react with nitrogen. Although there are rhenium nitrides, they are not formed by the direct action of nitrogen on the metal but through the interaction of rhenium chloride and ammonia.

Rhenium forms no carbides. The eutectic rhenium-carbon mixture melts at 2480° (Figure 194). In spite of the absence of a chemical reaction between rhenium and carbon, the heating of rhenium in contact with graphite is not recommended since the graphite diffuses into the metal and reduces its mechanical strength.

Rhenium reacts with fluorine and chlorine upon heating, but does not react for all practical purposes with bromine and iodine.

Rhenium is not attacked by cold or hot hydrochloric and hydrofluoric acids. It is dissolved by nitric acid, hot concentrated sulfuric acid, and hydrogen peroxide.

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Rhenium is not attacked by molten tin, zinc, silver, and copper but is attacked to a slight extent by aluminum and readily dissolves in molten nickel and iron.

As compared with tungsten, rhenium reacts to a much smaller extent with alumina at high temperatures and in vacuum.

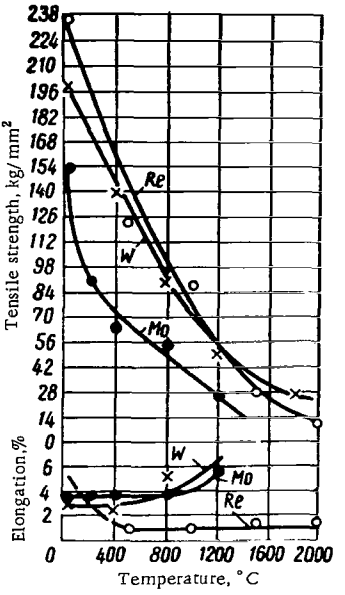

FIGURE 193. Tensile strength and elongation of forged rhenium (15% reduction in area), tungsten and molybdenum.

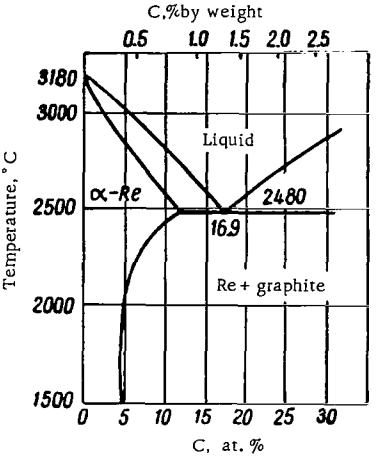

FIGURE 194. Phase diagram of the system rhenium-carbon.

The properties of rhenium compounds /1—3/

Of the rhenium compounds the most stable are those of heptavalent rhenium. In addition there are compounds in which rhenium has a valency of +6, 5, 4, 3, 2, and 1, as well as compounds in which Re has a valency of -1. The only compounds of technological importance are those in which rhenium has a valency of 7, 6, 4, or 3.

Oxides. Rhenium forms three stable oxides: rhenic anhydride Re_2O_7, rhenium trioxide ReO_3, and rhenium dioxide ReO_2.

Rhenic anhydride (or rhenium heptoxide) Re_2O_7 is formed when rhenium or some rhenium compound (e. g., the disulfide ReS_2) is oxidized in air. Rhenium heptoxide is bright-yellow. It melts at 297°and boils at 363°. The vapor pressures of Re_2O_7 at various temperatures are listed below:

Temperature, °C	50	100	150	200	250	280	300	325	360
P, mm Hg	$2.5 \cdot 10^{-8}$	$2.5 \cdot 10^{-5}$	$5.6 \cdot 10^{-3}$	0.35	10.9	61.2	160	312	711

Rhenic anhydride dissolves in water with the formation of rhenic acid $HReO_4$.

Rhenium trioxide ReO_3 is an orange-red solid, formed when a mixture of Re_2O_7 and rhenium powder is heated in a deficiency of air.

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The trioxide disproportionates in vacuo at temperatures above 400° by the reaction:

$$3ReO_3 \rightarrow ReO_2 + Re_2O_7.$$

Rhenium trioxide is sparingly soluble in water and in dilute sulfuric and hydrochloric acids. It has an appreciable volatility above 400°. The vapor pressure of ReO_3 at 350, 420, and 614° is 0.005, 0.288, and 0.76 mm Hg respectively /25/.

Rhenium dioxide ReO_2 is a dark-brown solid which is prepared by reduction of Re_2O_7 with hydrogen at 300° or by decomposition of ammonium perrhenate NH_4ReO_4 at 400° in an inert atmosphere (argon, nitrogen). Rhenium dioxide decomposes upon heating (above 750°) in vacuum, yielding rhenium and Re_2O_7:

$$7ReO_2 \rightarrow 2Re_2O_7 + 3Re.$$

The vapor pressure of ReO_2 at 650 and 750° is $1.3 \cdot 10^{-4}$ and $4.3 \cdot 10^{-3}$ mm Hg respectively /25/.

TABLE 63

The solubility of perrhenates in water

Salt	Solubility, g/l, at temperatures (°C)									
	18	19	20	21.5	24.6	28	30	80	89.5	93
$TlReO_4$	—	—	1.6	1.7	2.1	—	—	—	—	15.4
$CsReO_4$	—	7.8	—	—	—	—	—	—	—	—
$RbReO_4$	—	10.5	—	—	14.6	—	—	—	—	—
$KReO_4$	9.52	—	—	10.7	—	17.2	—	—	94.6	—
$Ba(ReO_4)_2$	—	—	53.2	—	—	85.9	—	—	—	—
NH_4ReO_4	—	—	62.3	—	—	—	86.4	323.4	—	—
$NaReO_4$	—	—	1000	—	—	—	—	—	—	—
$Mg(ReO_4)_2$	—	—	1679	—	—	—	1798	3141	—	—
$Ca(ReO_4)_2$	—	—	1776	—	—	—	1876	2600	—	—
$Cu(ReO_4)_2$	—	—	—	—	—	—	3245*	—	—	—

* Per 1000 g of water.

Rhenic acid and its salts (perrhenates). Rhenic acid $HReO_4$ is a strong monobasic acid. It is prepared by dissolving rhenic anhydride in water. In contrast to manganic acid, rhenic acid is not a strong oxidizing agent. The reaction between rhenic acid and carbonates, oxides or alkalies yields perrhenates. The perrhenates of thallium, potassium, and rubidium are sparingly soluble in water; ammonium and copper perrhenates are moderately soluble in water; the perrhenates of sodium, magnesium, and calcium are readily soluble in water (Table 63).

Rhenium chlorides. The chlorides most thoroughly studied are $ReCl_5$ and $ReCl_3$. Rhenium pentachloride is formed in the reaction between chlorine and rhenium metal at temperatures above 400°. It is a dark-brown solid. It melts at ~ 260 and boils at ~ 330°. It fumes in moist air as a result of hydrolysis. In water, $ReCl_5$ is decomposed by the reaction

$$3ReCl_5 + (8 + x)H_2O \rightarrow 2ReO_2 \cdot xH_2O + HReO_4 + 15HCl.$$

Rhenium pentachloride dissociates above 200° with the formation of $ReCl_3$. Rhenium trichloride is a reddish-black substance with a melting point of about 730°. It sublimes at 500 to 550°.

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There are two known rhenium oxychlorides: $ReOCl_4$ (mp 30°, bp 228°) and ReO_3Cl (mp 4.5°, bp 130°). The oxychlorides are formed by heating $ReCl_5$ or $ReCl_3$ to 150 to 400° in the presence of oxygen /1, 2, 21/.

Rhenium sulfides. Rhenium forms two sulfides — the heptasulfide Re_2S_7 and the disulfide ReS_2.

Rhenium heptasulfide is a dark-brown substance which is precipitated by hydrogen sulfide from both acid and alkaline solutions. From acid solutions, a satisfactorily quantitative precipitation is obtained at rather high acidities (4 N HCl or 6 N H_2SO_4). The precipitation of Re_2S_7 from alkaline solutions is slow; in order to obtain a quantitative precipitation, the solution is saturated with hydrogen sulfide and allowed to stand for several hours. Rhenium heptasulfide is sparingly soluble in solutions of the alkali metal sulfides.

Rhenium disulfide ReS_2 is prepared by thermal decomposition of Re_2S_7 (above 300°) or by direct interaction between rhenium and sulfur at 850 to 1000°. The crystalline lattice of the disulfide is hexagonal, like the lattice of molybdenite. The sulfide is black and has a density of 7.5. It is oxidized in air above 300°, yielding Re_2O_7. Rhenium disulfide is oxidized by nitric acid and hydrogen peroxide, yielding $HReO_4$ solution.

Uses of rhenium /3, 4, 6/

Rhenium and its alloys have already found some valuable uses. The most important of these are described below.

Production of electrical lamps and vacuum-tube devices. In this field, tungsten has been replaced by rhenium or rhenium-tungsten and rhenium-molybdenum alloys in some important uses. As compared with tungsten, rhenium has the advantages of a higher strength, retention of ductility in the recrystallized state, lower tendency to vaporization in the presence of traces of moisture (it is resistant to the so-called hydrogen-water cycle), a higher electrical resistance, and not having stable carbides.

These advantages of rhenium are of special importance in cases in which a long service life of the lamps and electronic devices is required, especially so under dynamic load conditions (e.g., in electronic tubes for radar in aviation, in photographic projection lamps, in lamps for railways, etc.). Rhenium and rhenium-tungsten alloys are used for the production of filaments, of cathode and heater cores, and the grid windings in radio tubes.

In contrast to tungsten, the recrystallized W + 30% Re alloy is fairly ductile at room temperature. The alloy Mo + 50% Re is also used in electronic devices. This alloy combines a high ductility (it can be cold worked) with a high strength. Since it has a lesser tendency (as compared with tungsten) to vaporize in the presence of traces of moisture, rhenium is used in discharge tubes filled with hydrogen containing water vapor.

The use of rhenium and its alloys in vacuum tube technology started only recently and its potential uses in this branch are by no means exhausted.

Thermocouples for high temperatures, made of rhenium and rhenium-tungsten or rhenium-molybdenum alloys, have a high, stable thermoelectromotive force.

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Thermocouples of (W + 5% Re) — (W + 20% Re) have been developed and are used in the USSR. Over the range 0 — 2500° the thermoelectromotive force of this thermocouple is a linear function of the temperature (see Figure 195). The thermoelectromotive force is 30 mV at 2000°. This thermocouple has the advantage of being made of electrodes which maintain their ductility after prolonged heating to high temperatures.

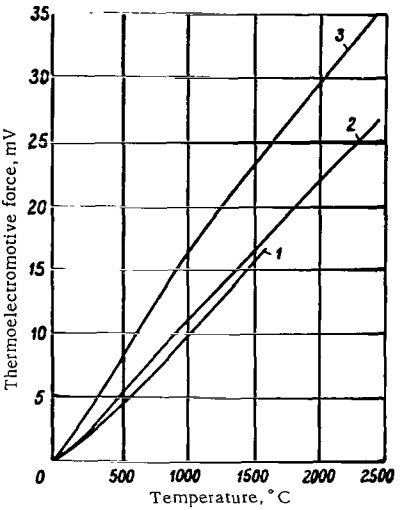

FIGURE 195. Thermoelectromotive forces of thermocouples made of rhenium-tungsten alloys and of a platinum thermocouple.

1 — Pt — Pt + 10% Re; 2 — W + 30% Re — W + 15% Re; 3 — W + 5% Re — W + 20% Re.

Electrical contacts. Rhenium and rhenium-tungsten alloys are characterized by their high resistance to wear and electroerosion under the conditions of an electric arc. Investigations have shown that when used as a contact material rhenium and rhenium-tungsten alloys are preferable to tungsten as regards their resistance to atmospheric corrosion and corrosion under tropical conditions, as well as for their more constant contact conductivity under the effect of elevated temperatures and contact arcs. The great effectiveness of the use of rhenium contacts in ship magneto generators has been reported. Tests of contacts made of an alloy of W + 15% Re have shown that they are superior to tungsten contacts when used in voltage regulators and ignition devices.

Production of heat-resistant and refractory alloys. Extensive research is carried out to evaluate the possibility of using rhenium as an alloying additive which improves the refractoriness of alloys, including rhenium-based refractory alloys for aviation and missile making. The phase diagrams of the systems rhenium-refractory metals are shown in Figure 196 /9, 10/.

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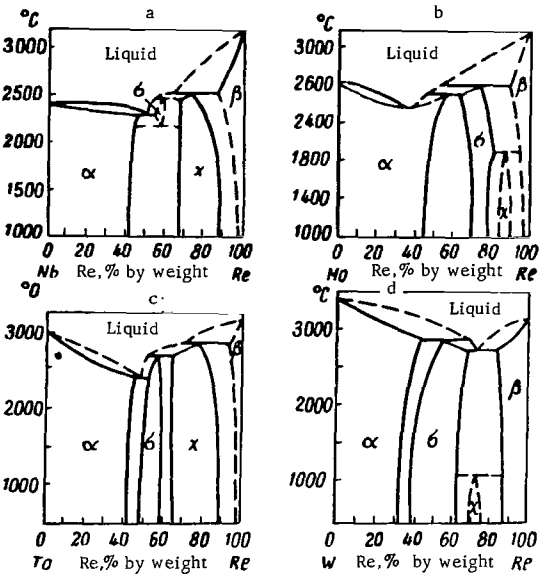

FIGURE 196. Phase diagrams of the systems rhenium—refractory metals.

a—Nb—Re; b—Ta—Re; c—Mo—Re; d—W—Re.

Instrumentation. Rhenium and its alloys are characterized by their great hardness and wear resistance. As a result, their use in the manufacture of instruments, e.g., for balance supports, axes for geodetic apparatus (compasses, etc.), tip bearings, springs, etc., is very promising. Performance tests of flat rhenium springs after a large number of heating (to 800°) cycles have shown the absence of deformation and conservation of strength.

100. OCCURRENCE

The concentration of rhenium in the Earth's crust is very low — 10^{-7}% by weight. Rhenium is a typical scattered element. The existence of three rhenium minerals has been reported: the oxide, the sulfide, and copper sulforhenate (dzhezkazganite). However, none of these has been isolated. Rhenium at concentrations higher than its average concentration in the Earth's crust has been found in granitic pegmatites and in pneumatolithic formations. Higher rhenium concentrations have been found in columbites, tantalites, zirconates (alvite), minerals of the yttrium and erbium earths (thortveitite, gadolinite), copper sulfides, and especially in molybdenite. At present, molybdenite is the main source of the production of rhenium.

The association of rhenium with molybdenum is caused by the isomorphism of MeS_2 and ReS_2 (the ionic radii of tetravalent molybdenum and tetravalent rhenium are 0.68 and 0.56 Å respectively).

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The rhenium concentration in molybdenites from various deposits is within 10^{-2}—10^{-5}%. Molybdenites from copper-molybdenum deposits have the higher rhenium contents. Thus, molybdenite from the copper slate deposits of Mansfeld (German Democratic Republic) contains 0.01% rhenium. The molybdenite concentrates from copper-molybdenum deposits in the USSR contain 0.025 to 0.04% rhenium. In addition to molybdenite concentrates, some copper sulfide concentrates also serve as a source of rhenium /3/.

Behavior of rhenium in the processing of molybdenite concentrates /3, 8, 12, 22, 23/

Molybdenite concentrates are usually subjected to oxidizing roasting at 550 to 600°, which usually produces a calcine containing molybdenum trioxide and some impurities. The rhenium initially present in the molybdenite is converted to the heptoxide Re_2O_7 which is entrained with the gas stream (the bp of Re_2O_7 is 363°). The degree of vaporization of the rhenium depends on the roasting conditions and the mineralogical composition of the concentrate.

Thus, in one plant in the USSR vaporization of about 65 to 75% of the rhenium resulted from roasting low-quality molybdenite concentrates on the sole of a muffle furnace with manual raking of the material. The calcine contained 35 to 25% of the rhenium. The nonquantitative vaporization of the rhenium on roasting in a muffle furnace could be attributed to the partial interaction of Re_2O_7 with calcite as well as with iron and copper oxides, yielding perrhenates. Calcium perrhenate may be formed in the reaction:

$$CaCO_3 + Re_2O_7 \rightarrow Ca(ReO_4)_2 + CO_2.$$

In the case of a defficiency of air (e.g., inside sintered particles) the reaction between Re_2O_7 vapor and MoS_2 may lead to the formation of rhenium trioxide and dioxide /22/:

$$6Re_2O_7 + MoS_2 = 12ReO_3 + MoO_2 + 2SO_2;$$
$$2Re_2O_7 + MoS_2 \rightarrow 4ReO_2 + MoO_2 + 2SO_2.$$

Soviet investigators have found that the highest degree of volatilization of the rhenium is obtained by roasting the molybdenite concentrates in a fluidized bed; the degree of volatilization of the rhenium is 92 to 96%. This is attributed to the fact that the side-reactions of perrhenate formation occur to a lesser degree in fluidized-bed roasting, and the formation of the lower rhenium oxides is impossible /12/. Effective collection of the rhenium from the gaseous phase may be accomplished only by using wet dust-collecting systems (scrubbers, bubblers, wet electrostatic filters). No more than 20 to 30% of the rhenium is collected in the dust-collecting equipment commonly used in molybdenite concentrate roasting plants (dust chambers, cyclones, electrostatic filters). When molybdenite concentrates are roasted in fluidized-bed furnaces, up to 30 to 45% of the material to be roasted is entrained with the gases. The cyclones collect up to 95% of the dust, hence the temperatures in the cyclones must not be allowed to drop below 400° in order to prevent condensation of rhenium oxide. Nevertheless, the dust collected in the electrostatic filters contains 0.1 to 1.5% rhenium.

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When using wet dust-collecting methods, most of the rhenium is collected in the acid solutions. To increase the rhenium concentration, the solution is returned several times to the wet dust-collector (i. e., the solution is recycled). The solutions withdrawn from the wet dust-collecting system contain 0.2 to 0.8 g Re/l and 30 to 60 g H_2SO_4/l.

In the case of a nonquantitative volatilization of the rhenium during the roasting of molybdenite concentrates, the rhenium remaining in the cinders passes together with the molybdenum into the sodium carbonate or ammonium hydroxide solutions (during the leaching of the cinders), but remains in the mother liquor after precipitation of the molybdenum compounds.

Thus, in the processing of molybdenite concentrates, rhenium may be produced from the dusts obtained in the roasting of the concentrates, from the acid solutions of the wet dust-collectors, and from the mother liquor (waste solution) after the hydrometallurgical processing of molybdenite cinders.

Behavior of rhenium in the production of copper /3/

In the production of copper matte by smelting of copper concentrates in shaft furnaces, a fraction (30 to 50%) of the rhenium is volatilized (together with the zinc, lead, cadmium, thallium, germanium, and selenium) mainly as the sulfides, and passes into the collected dusts. As an example, we list below the composition of the dusts obtained in the shaft-furnace smelting of copper ores from the Mansfeld deposit in the German Democratic Republic (in%):

Zn	21	Ga	0.0013
Pb	18.02	Ag	0.0738
Cu	0.84	Si	0.015
Cd	0.12	S	17.2
Se	0.06	Cl	0.92
Re	0.043	Bitumen (organic substance)	6.67
Ge	0.0073		

Up to 75% of the rhenium is volatilized during the smelting of copper concentrates in reverberatory furnaces, and all the rhenium initially present in the matte is expelled with the gases during the blowing of the matte in converters. Thus, in the processing of copper concentrates the rhenium should accumulate in the dusts of the shaft and reverberatory furnace smelting and in the converter dusts. When the furnace and converter gases are used for the production of sulfuric acid, the rhenium accumulates in the sulfuric acid circulating in the electrostatic filters.

101. EXTRACTION OF RHENIUM FROM THE VARIOUS WASTES FORMED IN THE PROCESSING OF MOLYBDENITE CONCENTRATES

Various methods are used for the extraction of rhenium from rhenium-containing materials (dusts, solutions), depending on the nature and composition of the materials.

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In the dusts from the roasting of molybdenite concentrates the rhenium is present mainly as Re_2O_7, which makes it possible to extract it by leaching with water. Since a fraction of the rhenium in the dusts may be present as a component of the lower oxides (which are sparingly soluble in water), the leaching is carried out in the presence of oxidizing agents, e.g., pyrolusite. The leaching of the dusts is occasionally preceded by certain pyrometallurgical operations: roasting with sublimation (in order to increase the rhenium concentration in the dust) or roasting with the addition of lime (to bind the MoO_3 as calcium molybdate $CaMoO_4$). During the subsequent leaching with water, the sparingly soluble calcium molybdate is separated from the calcium perrhenate $Ca(ReO_4)_2$ which is extracted into the solution.

The following methods may be used to extract the rhenium from the solutions obtained in the leaching of the dusts, the solutions from the wet dust-collecting systems, and the mother liquors remaining after the precipitation of molybdenum compounds:

1) precipitation as a sparingly soluble compound (potassium perrhenate $KReO_4$, rhenium sulfide Re_2S_7);
2) sorption on ion exchange resins or activated carbon;
3) extraction with organic solvents.

The last two methods are used to prepare more concentrated solutions, from which the rhenium is then precipitated as potassium or ammonium perrhenates, which are the main starting materials for the production of rhenium. Some technological processes which make use of the various methods for the extraction of rhenium from manufacturing wastes are described below.

Extraction of rhenium from the electrostatic filter dust

The dust collected in electrostatic filters contains 0.4 to 1.5% Re. The dust is composed mainly of molybdenum compounds (MoO_3, MoS_2). The dust usually contains a large amount of sulfuric acid since the roasting gases contain SO_3 and water vapor.

A flow sheet showing the dust-processing method used at one Soviet plant is presented in Figure 197 /15/. The dust is leached twice with hot water at a solid : liquid ratio of 1 : (2.5 to 3), with the addition of finely ground pyrolusite to the solution, in order to oxidize the lower rhenium compounds. The insoluble residue is separated by filtration in suction filters or filter presses. The combined solutions and wash waters contain 0.5 to 0.6 g Re/l, 8 to 10 g Mo/l, 20 to 30 g H_2SO_4/l, and some $CuSO_4$ and $Fe_2(SO_4)_3$.

In order to separate most of the molybdenum as well as the copper and iron, the solution is neutralized to pH 11 to 12 with milk of lime, and heated (with stirring) to 60 to 70°. The precipitate formed contains calcium sulfate and molybdate, and copper and iron hydroxides. The losses of rhenium with the washed precipitate are insignificant. The solutions are evaporated in stainless-steel evaporators to a rhenium content of 15 to 20 g/l. The solution is filtered and potassium perrhenate is precipitated by heating the solution and adding potassium chloride (about 50 to 60 g of KCl per liter of solution). The solution is allowed to cool and a crystalline precipitate consisting of technical potassium perrhenate is separated.

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The degree of precipitation of the rhenium is 98 to 99%. The mother liquor contains 0.02 to 0.5 g Re/l. The rhenium may be extracted from the mother liquor by sorption on resins. The technical potassium perrhenate is purified by several successive recrystallizations.

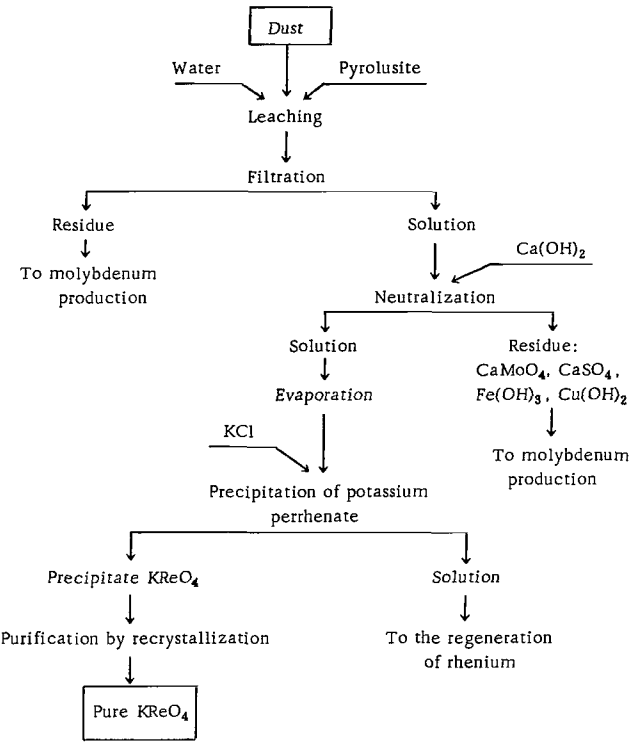

FIGURE 197. Flow sheet of the extraction of rhenium from the dust collected in the electrostatic filters in the manufacture of molybdenum.

The solubility of $KReO_4$ in water at 90 to 100° is about 100 g/l and at 20° it is 10 g/l. Thus, the yield of crystals in the recrystallization may be about 90%. The yield may be increased to 95% by cooling the solution to 5°. The recrystallization may be carried out according to the flow sheet shown in Figure 198. The mother liquors from the first three recrystallizations, which contain the accumulated impurities, are evaporated to dryness, treated with water, and the aqueous solution (which contains the potassium perrhenate) is returned to the first crystallization stage. The solutions from the last recrystallizations are returned to the first crystallization stage. The total degree of extraction of rhenium from the dusts into the recrystallized potassium perrhenate is 85%.

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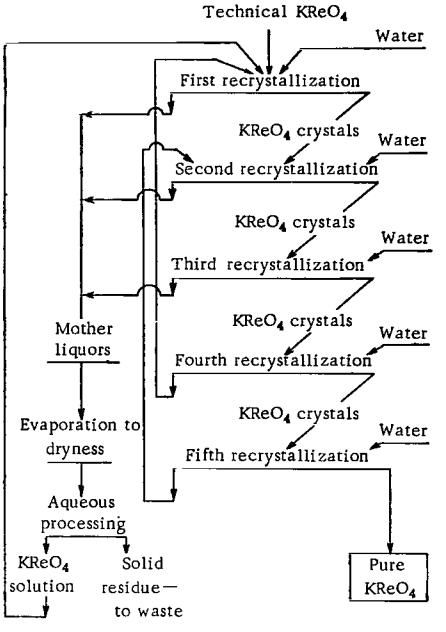

FIGURE 198. Flow sheet of the purification of potassium perrhenate by recrystallization.

Another variant of the dust processing process, which was developed by Soviet investigators /3/, involves a preliminary roasting of the dust with lime at 570 to 670°. The dust is mixed with slaked lime at a ratio of 3 : 2 (by weight) and roasted on the sole of a muffle furnace for 2 to 4 hours. The product is then leached with water at 70 to 80°, at a solid : liquid ratio of 1 : 3. In order to increase the rhenium concentration, one solution is used for the successive leaching of six portions of the roasted product, as shown in Figure 199. The wash waters are combined with the main solutions and forwarded to evaporation, but a fraction of the combined solution is returned to the leaching cycle.

Potassium perrhenate is isolated from the evaporated solutions, as described above.

Sorption of rhenium from solutions of low rhenium content

In the processing of low-grade molybdenite concentrates to calcium molybdate by the scheme described in the chapter on molybdenum (see p. 90), the rhenium remains in the mother liquor from the precipitation of the calcium molybdate. The approximate composition of the liquor is (in g/l):

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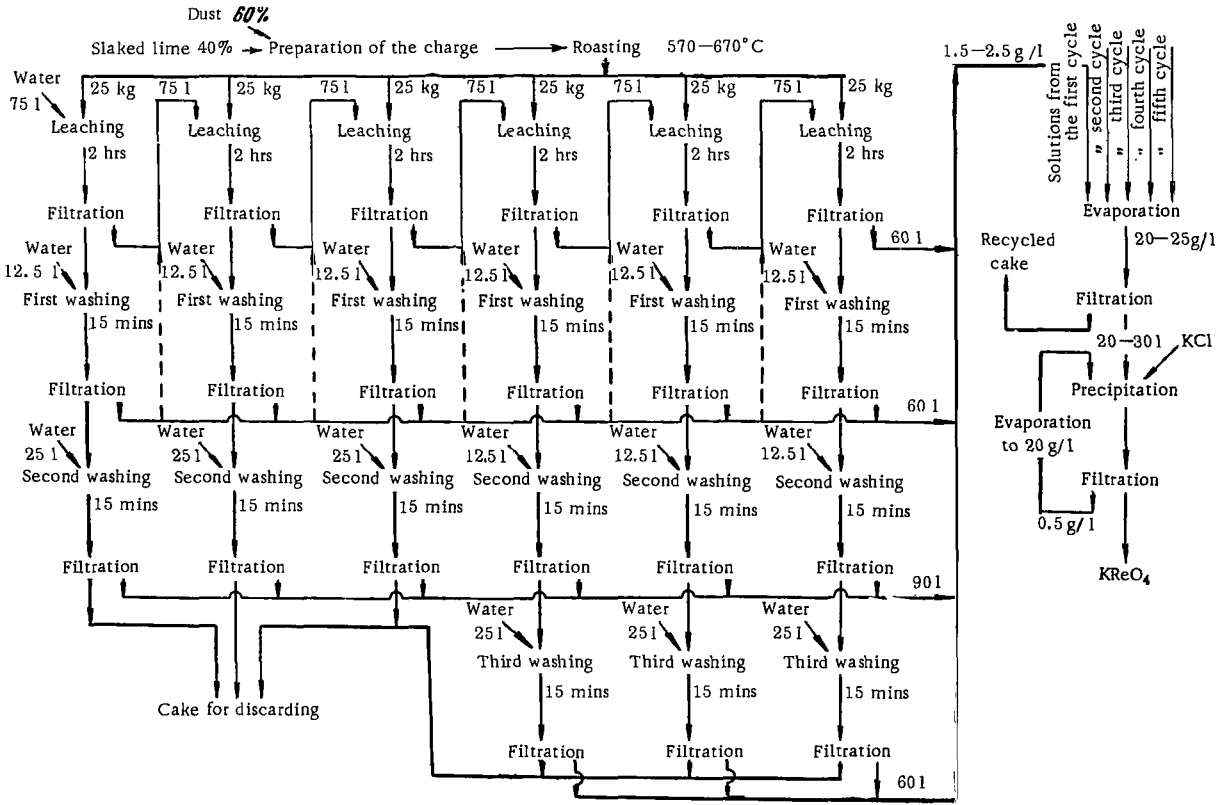

FIGURE 199. Flow sheet of the extraction of rhenium from the dust, including roasting with lime.

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Re	0.015—0.04	ClO_3^-	0.7—1.3
Mo	0.4—0.9	Na	28—35
Cl^-	27—30	pH of the solution	8.5—8.7
SO_4^{2-}	15—35		

The molybdenum and the rhenium are extracted from the above solution by selective sorption of the molybdenum ions on an anion exchange resin followed by the sorption of rhenium on activated carbon (Figure 200) /3/. The solution is acidified to pH = 3 and heated to expel the carbon dioxide (the starting solution contains sodium carbonate). The cold filtered solution is then passed through an ion exchange column filled with the anion exchange resin "Espatite AN-1" in the sulfate form. The grain size of the resin is 0.15 to 0.6 mm. In the weakly acid solution the molybdenum is present as the anion of isopolyacids (e.g., $[Mo_4O_{13}]^{2-}$ anions) which are sorbed on the resin. The capacity of the resin for molybdenum is about 20%. The filtration rate is about 5 volumes of solution per one volume of resin per hour. After the saturation of the resin the molybdenum is eluted with a solution of ammonium hydroxide. The resin is then charged again with SO_4^{2-} ions, which is accomplished by passing sulfuric acid (18 g/l) through the column.

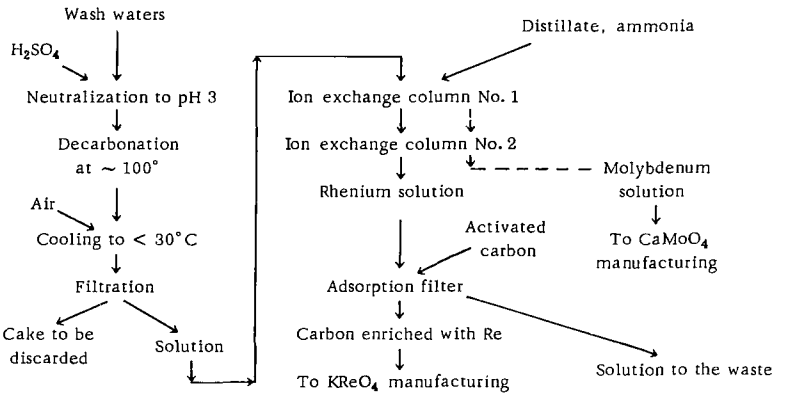

FIGURE 200. Flow sheet of the extraction of rhenium from the mother liquors in manufacture of calcium molybdate.

The ReO_4^- ions undergo almost no sorption on the anion exchange resin AN-1 from weakly acid solutions, and these ions remain in the filtrate (which contains 15 to 40 mg Re and 10 to 20 mg Mo per liter). The solutions are then passed through adsorption filters packed with activated carbon (brand KAD, particle size 0.1 to 0.8 mm), which sorbs quantitatively the rhenium and molybdenum from the solution. The capacity of the carbon for rhenium (in the case of a rhenium concentration in the solution of up to 20 mg/l) is low, i.e., about 2%. By selective desorption the molybdenum may be desorbed first from the carbon (with a cold 1% solution of Na_2CO_3),

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followed by the rhenium (which is desorbed with a sodium carbonate solution heated to 90°). The rhenium concentration in the solution is 200 to 400 mg/l. More concentrated solutions are obtained by repeating the sorption on the carbon. The final solutions are treated to precipitate the rhenium as potassium perrhenate.

More effective ion exchange methods for the extraction of rhenium from the solutions coming from the dust-collecting systems have been recently developed. Strongly basic anion exchange resins are used for the sorption. The ReO_4^- and MoO_4^{2-} ions are adsorbed together on the resin from nearly neutral solutions. The molybdenum is then eluted with a ~ 10% alkaline solution, followed by the rhenium which is eluted with a ~ 7 N solution of hydrochloric or perchloric acid /19/.

102. PRODUCTION OF RHENIUM

The existing rhenium production methods may be divided as follows:

1) reduction of potassium or ammonium perrhenate with hydrogen;
2) reduction of rhenium dioxide with hydrogen;
3) electrodeposition of rhenium from aqueous solutions;
4) thermal dissociation of rhenium halides.

The last two methods are used mainly for the application of rhenium coatings.

Reduction of potassium perrhenate with hydrogen

The final product in the extraction of rhenium from various products enriched in rhenium is usually potassium perrhenate. As could be expected, rhenium was produced at first by reduction of this salt with hydrogen, as follows:

$$KReO_4 + 3^1/_2H_2 \rightarrow Re + KOH + 3H_2O.$$

The reduction was usually carried out in two stages. After a first reduction at 500 to 550° the reduction product was washed several times with water to remove the hydroxide. The powder was then subjected to a second reduction at 900 to 1000°, washed first with dilute hydrochloric acid and then with water, and dried in vacuum or in a current of hydrogen.

Even after the two-fold reduction of potassium perrhenate with hydrogen and the washing with acid, the rhenium powder obtained still contains at least a few hundredths of one percent of potassium /14/. Now a potassium content above 0.006% interferes with the sintering of rhenium bars (the maximum density which can be obtained is 60 to 70% of the theoretical), which causes brittleness of the metal and makes it impossible to work it under pressure /18/. Thus, the reduction of potassium perrhenate with hydrogen at present is used only for the production of technical grade rhenium powder.

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Reduction of ammonium perrhenate with hydrogen

The reduction of ammonium perrhenate with hydrogen is the most common method for the production of pure rhenium powder; this is then converted into dense bars which can be worked by pressure.

Production of ammonium perrhenate

Most of the ammonium perrhenate is produced from potassium perrhenate by various methods which are described briefly below.

A method based on the sublimation of rhenium heptoxide Re_2O_7 was developed at the Battelle Institute in the USA /11/. The potassium perrhenate is reduced at first with hydrogen at 500° and the product is washed with water yielding technical grade rhenium powder. The powder is oxidized with oxygen at 800° in a quartz tube. The rhenium heptoxide is sublimed and condensed at the cold end of the tube. It is dissolved in a small amount of water and ammonium perrhenate is precipitated by neutralizing the solution with ammonia. The mother liquor is evaporated in order to extract the residual rhenium. The precipitated ammonium perrhenate is contaminated with iron hydroxide. To remove the iron, the salt is dissolved in a dilute solution of ammonium hydroxide. The solution is then evaporated and ammonium perrhenate is crystallized.

The yield of rhenium as ammonium perrhenate is 85%, the remaining rhenium being subsequently extracted from the mother liquors and wash waters. The total amount of impurities in the ammonium perrhenate produced by the method is about 0.02%.

The ion exchange method was proposed in the USSR by Kovyrshin /13/. When a solution of potassium perrhenate is passed through a cation exchange resin (in the hydrogen or ammonium form) and exchange reaction takes place with the formation of a solution of rhenic acid or ammonium perrhenate:

$$[\mathrm{Cat.}]\,H + KReO_4 \rightarrow [\mathrm{Cat.}]\,K + HReO_4;$$
$$[\mathrm{Cat.}]\,NH_4 + KReO_4 \rightarrow [\mathrm{Cat.}]\,K + NH_4ReO_4.$$

Thus, ion exchange on a cation exchange resin may yield a solution of either rhenic acid or ammonium perrhenate. The Soviet-made cation exchange resin KU-2 may be used for the purpose. Another variant of the method involves the use of anion exchange resins, which absorb the ReO_4^- ions which are then eluted with ammonium hydroxide.

The above method yields ammonium perrhenate containing 0.01 to 0.005% K.

The extraction method involves the extraction of rhenic acid from an acidified solution of potassium perrhenate with an organic solvent, followed by the reextraction of rhenic acid from the organic phase by a solution of ammonium hydroxide. Tributyl phosphate (the use of which was proposed by Soviet scientists — Bibikova et al.) and other organic solvents may be used for the extraction. The rhenium is reextracted from the organic phase with a solution of ammonium hydroxide, and ammonium perrhenate is then isolated from the solution /24/.

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The sulfide method. Potassium perrhenate is dissolved in hot 10% HCl. Hydrogen sulfide is bubbled through the solution, resulting in the precipitation of rhenium sulfide Re_2S_7. The sulfide is suspended in a 10% solution of ammonium hydroxide and is oxidized with hydrogen peroxide. This yields a solution containing ammonium perrhenate and ammonium sulfate:

$$Re_2S_7 + 16NH_4OH + 28H_2O_2 \rightarrow 2NH_4ReO_4 + 7(NH_4)_2SO_4 + 36H_2O$$

The solution is evaporated and ammonium perrhenate is crystallized. The presence of ammonium sulfate causes a sharp drop in the solubility of ammonium perrhenate (to about 5 g/l), which makes it possible to isolate the bulk of the rhenium from the solution.

Reduction

Ammonium perrhenate produced by one of the above methods usually contains 0.01 to 0.005% potassium and small amounts of iron, silicon, aluminum, and other elements.

In order to produce a fine rhenium powder, the ammonium perrhenate is ground before the reduction in rubber-lined rotary mills using rhenium bar fragments as the milling medium. The ground ammonium perrhenate is reduced by hydrogen in tubular furnaces. The salt is placed in a thin layer (6 to 8 mm) into molybdenum or nickel-molybdenum boats. The salt is first dried in a current of hydrogen for one hour at 300°. It is then reduced by heating for 1 to 2 hours at 800°. The resulting powder has a particle size of 1 to 25 μ. The approximate chemical composition of the powder is shown in Table 64.

TABLE 64

Approximate composition of rhenium powders produced by different methods, %

Element	From $KReO_4$	From NH_4ReO_4	From ReO_2 produced by the decomposition of $ReCl_5$
Fe	0.02	0.0025	0.012
Al	0.002	0.0015	0.008
Mo	0.001	< 0.0005	Not found
Ni	0.028	0.0015	" "
Cu	0.0035	0.0015	0.0002
K	0.04	0.005	Not found
Na	0.06	0.005	" "
Ca	0.1	0.006	0.002
Pb	0.002	0.0001	Not found
Sn	0.0006	< 0.0001	—
Cd	< 0.001	< 0.0001	—
Mg	—	—	0.005
Si	—	—	0.015

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Reduction of rhenium dioxide by hydrogen /11/

The method was developed at the Battelle Institute in the USA and is known as the "chloride method" since the pure rhenium dioxide is produced from the chloride. Technical grade rhenium produced by the reduction of potassium perrhenate with hydrogen, or rhenium scrap from mechanical working, or precipitates formed in the regeneration of rhenium from mother liquors may serve as the starting material. The starting material is first heated for one hour in a current of hydrogen at 1000° (in order to reduce the oxides) and is then chlorinated with chlorine at 750° to produce $ReCl_5$ which is then distilled (its bp is 330°). The resulting chloride is decomposed with cold water (at a temperature not exceeding 10°). Hydrated rhenium dioxide is the main reaction product (about 70% Re):

$$3ReCl_5 + (8 + x)H_2O \rightarrow 2ReO_2 \cdot xH_2O + HReO_4 + 15HCl.$$

As is evident from the above reaction, a fraction of the rhenium remains in the solution as rhenic acid. In addition, the solution contains a very small amount of chlororhenic acid H_2ReOCl_5.

In order to facilitate the separation of the hydrated dioxide precipitate by filtration, carbon dioxide is bubbled through the suspension for thirty minutes prior to the filtration. The precipitate ($Re_2O \cdot xH_2O$) is separated by filtration in a centrifuge and is dried in a vacuum. In order to extract the rhenium remaining in the filtrate, its lower forms are oxidized with hydrogen peroxide to $HReO_4$, the solution is neutralized with ammonium hydroxide, and ammonium perrhenate is isolated and returned to the reduction cycle. The rhenium dioxide is reduced with hydrogen in molybdenum boats (in a layer $\sim$ 20 mm thick) by holding first for one hour at 400°, then for one hour at 600°. The slightly sintered powder is crushed and subjected to further reduction for 2 hours at 800°. The total yield of rhenium by the above method is 95%. The use of the above method yields rhenium virtually free of alkali metals and most other elements except iron and silicon (see Table 64).

Reduction of potassium perrhenate in a solution by hydrogen under pressure /17/

The increased potassium content of rhenium produced by the reduction of solid potassium perrhenate with hydrogen is attributed to the fact that at the high reduction temperatures a small fraction of the potassium enters the crystal lattice of the rhenium. Hence, it could be expected that a more thorough removal of the potassium could be achieved by reducing the $KReO_4$ in an aqueous solution by hydrogen under pressure.

Soviet workers found that at a partial hydrogen pressure of 60 atm and a temperature of 200°, the rhenium can be precipitated quantitatively (as a mixture of the metal and the lower oxides) from solutions containing up to 100 g $KReO_4$/liter:

$$KReO_4 \text{ (solution)} + 3^1/_2H_2 \rightarrow Re + KOH + 3H_2O.$$

The precipitates are washed with dilute hydrochloric acid and water and are reduced with hydrogen at 850 to 900°.

The rhenium powder produced by this method contains 0.004 to 0.006% potassium, i.e., its potassium content is the same as that of the powder produced from ammonium perrhenate. The main advantage of the autoclave process is that it involves a small number of stages since the conversion of potassium perrhenate into ammonium perrhenate need not be carried out.

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Production of rhenium powder by electrolysis /4, 24/

The electrodeposition of rhenium from a solution is used primarily for the application of rhenium coatings. However, it may also be used to produce rhenium powder.

Potassium or ammonium perrhenate may be used for the electrolysis; two bath compositions have been recommended, depending on the salt used (the concentrations are in g/l):

	First	Second
Ammonium perrhenate	—	100
Potassium perrhenate	50	—
Sulfuric acid	75	100
Ammonium sulfate	40	60

For either of the two baths, the electrolysis is carried out under the following conditions: cathode current density 100 to 200 amp/dm^2, bath temperature 75°. The electrolysis is carried out at a constant rhenium concentration in the electrolyte, and the electrolyte is circulated continuously. Platinum anodes and tantalum plate cathodes are used in small-scale electrolysis.

The mechanism of the electrolysis probably involves the initial discharge of hydrogen ions on the cathode, yielding atomic hydrogen which then reduces the ReO_4^- ions:

$$7H^+ + 7e \rightarrow 7H;$$
$$ReO_4^- + 7H \rightarrow Re + OH^- + 3H_2O;$$
$$\overline{ReO_4^- + 7H^+ + 7e \rightarrow Re + OH^- + 3H_2O}.$$

The cathodes are periodically withdrawn and the rhenium deposit removed. The deposit is washed with water, with dilute hydrochloric acid, then again with water and is dried.

The yield of rhenium when using potassium perrhenate is 90 to 95%, and when using ammonium perrhenate it is 93 to 98%. The current efficiency is 25 to 27 and ~35% respectively.

The approximate concentrations of impurities in electrolytic rhenium are as follows: 0.002% Cu, 0.002% Fe, 0.003% Mo, 0.005% Ca, < 0.003%Al, 0.0015% Na, and 0.005%K when using ammonium perrhenate or 0.03% K when using potassium perrhenate.

As compared with the powder produced by reduction of perrhenates with hydrogen, electrolytic rhenium has a coarser particle size. Its conversion into a dense, ductile metal by powder metallurgy techniques is difficult.

Thermal dissociation of the halides

Rhenium of a high degree of purity may be prepared by thermal dissociation of rhenium pentachloride $ReCl_5$ or oxychloride $ReOCl_4$ on a heated tungsten or rhenium filament /20, 26/. This method is used mainly for the coating of tungsten and molybdenum with rhenium.

Rhenium pentachloride (bp 330°) is produced by the reaction between chlorine and metallic rhenium at 500 to 600°. The thermal dissociation is carried out in a vessel made of fire-resistant glass and containing the electrically heated tungsten or rhenium filament. The dissociation is carried out in vacuo (with the evacuation of the chlorine formed in the reaction) or in a protective atmosphere (nitrogen, argon) which acts as a carrier of the rhenium pentachloride vapor. The surface of the filament is heated to 1200 to 1300°.

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Rhenium coatings on tungsten, which are produced by this method, adhere strongly to the base metal. Soviet workers /20/ developed a method for the coating of tungsten and molybdenum with rhenium by thermal decomposition of rhenium oxychloride $ReOCl_4$. Rhenium oxychloride has the following advantages over rhenium pentachloride: in contrast to $ReCl_5$ (which dissociates at 200° from the solid state to chlorine and the nonvolatile rhenium trichloride $ReCl_3$), rhenium oxychloride is not decomposed upon heating up to 600°. This makes it possible to maintain a high concentration of $ReOCl_4$ in the vapor phase ($ReOCl_4$ boils at 228°). The rate of deposition of rhenium on a metallic surface heated to 1200 to 1300° is $\sim 160\ mg/cm^2 \cdot$ hour, i.e., 16 times higher than the rate of deposition from $ReCl_5$. Rhenium oxychloride is decomposed with the production of rhenium by the reaction

$$3ReOCl_4 \xrightarrow{1200-1300°C} 2Re + ReO_3Cl + 3^1/_2Cl_2.*$$

The volatile ReO_3Cl is expelled together with the chlorine. The theoretical yield of rhenium in the above reaction is 66% but the actual yield is 50 to 60%.

The oxychloride is produced through the oxidation of $ReCl_5$ at 150 to 180° in a current of oxygen. Rhenium oxychloride is readily purified by rectification.

A diagram of an apparatus for the continuous coating of tungsten wire with rhenium is shown in Figure 201.

103. PRODUCTION OF SOLID RHENIUM /15, 16, 18/

Solid rhenium is produced by powder metallurgy techniques. Rhenium powders have a particle size of 1 to 5 μ (average $\sim 2\mu$) and their bulk weight is about 2.25 g/cm^3. To produce the solid metal, the powder is pressed in steel dies under a pressure of 4 to 5 $tons/cm^2$, yielding rectangular bars (12 × 12 mm) with a density of about 9.5 g/cm^3 ($\sim$ 45% of the theoretical). The bars are subjected to an advance sintering (with the purpose of achieving a certain reinforcement and of removing a fraction of the volatile impurities) for 2 hours at 1200° either in vacuum (0.5 to 1 μ pressure) or in hydrogen. The high temperature sintering is carried out in hydrogen, in the equipment used for the sintering of tungsten bars. The maximum sintering temperature is 2800 to 2850°. The degree of contraction during the sintering depends on the concentration of volatile (under the sintering conditions) impurities. The main such impurities are the alkali metals. The effect of the potassium concentration on the contraction can be seen from the following data:

Potassium concentration, %	<0.006	0.02—0.05	0.06—0.1	>0.1
Density of the sintered bar, % of the theoretical	>90	80—88	70—80	65—75

Copper is a harmful impurity (although the maximum permissible copper content is higher than the maximum permissible potassium content) which is volatilized under the sintering conditions. The effect of other impurities on the contraction of the bars during the sintering has not been studied in sufficient detail.

The sintered bars, whose density must be at least 18.9 g/cm^3 ($\sim$ 90% of the theoretical density of rhenium) are then made more dense by forging or cold rolling with an intermediate annealing. Hot-working (which is used for tungsten and molybdenum) is not used in the case of rhenium since rhenium suffers from hot brittleness caused by the formation of the low-melting rhenium heptoxide on the grain boundaries.

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* [*sic.*]

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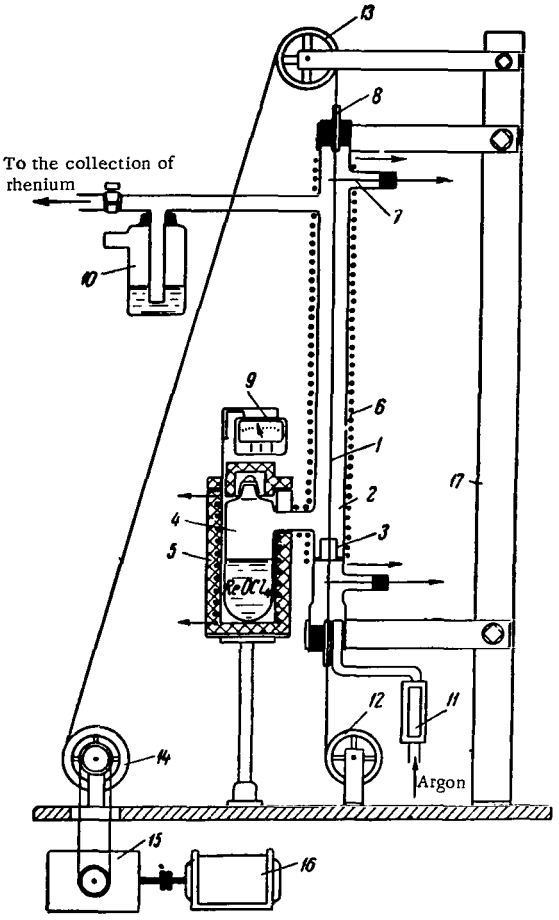

FIGURE 201. Diagram of an apparatus for the continuous coating of tungsten wire with rhenium.

1—tungsten wire; 2—glass tube; 3—quartz shield; 4—evaporator for the rhenium oxychloride; 5—heater for the evaporator; 6—coiled heater for the tube walls; 7—sliding contacts for the supply of current to the wire; 8—capillaries; 9—thermocouple with galvanometer; 10—hydraulic closure; 11—argon flowmeter; 12—14—rewinding spools; 15—reducing gear; 16—motor; 17—support.

The mechanical working of rhenium is complicated by the fact that rhenium has a very high deformation resistance. Even a small (5 to 10%) reduction in area in the cold causes a sharp increase in its Vickers hardness, from 250 to 300 to 800 kg/mm^2. Thus, cold-working is followed by annealing for 30 to 60 minutes at 1700 to 1800° after which the cold-working may be continued.

Rhenium is rolled with relative ease. Foils with a thickness as low as 25 μ may be produced. The drawing of the metal is more difficult. Wires may be drawn to a diameter of 75 μ.

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In addition to the powder metallurgy techniques, melting in arc or electron beam furnaces may also be used for the production of solid rhenium. Thorough purification of the rhenium may be accomplished by zone melting in a high vacuum.

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Part Four

THE LIGHT RARE METALS

Chapter XII

BERYLLIUM

104. GENERAL DATA ON BERYLLIUM

The element beryllium was discovered in 1798 by the French chemist Vauquelin, who was trying to prove that the chemical compositions of the precious stones beryl and emerald were identical. Beryllium metal was prepared for the first time in 1828 by Wöhler in Germany and Bussy in France through the reduction of beryllium chloride with potassium. It was not known until the 1870's whether beryllium was divalent or trivalent. Only Mendeleev was able to determine decisively the position of beryllium as belonging to Group II of the periodic table and thus to corroborate the opinion of the Russian chemist Avdeev who considered BeO as a magnesium-type (i.e., divalent) oxide and who was the first to determine the atomic weight of beryllium (in 1842). In 1898 Lebeau (in France) prepared pure (99.5 to 99.8%) beryllium by electrolysis in molten media.

Properties of beryllium

Beryllium belongs to Group II of the periodic system. The metal is light-gray when solid and dark-gray when in powdered form. Beryllium is one of the lightest metals. The main physical properties of beryllium are listed below:

Atomic number	4
Atomic weight	9.013
Density, g/cm^3	1.847
Crystalline lattice:	
α-Be (< 1250—1260°C)	Close-packed hexagonal
β-Be (> 1250—1260°C)	Body-centered cubic
Lattice parameters of α-Be, A:	
a	2.281
c	3.576
c/a	1.568
Melting point, °C	1283
Boiling point, °C	2970
Heat of fusion, cal/g	250—275
Heat of vaporization, cal/g	593
Specific heat at 100°C, cal/g °C	0.481
Heat conductivity (cal/cm·sec, °C) at:	
0°C	0.355—0.36
600°C	0.21—0.24

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Thermal expansion coefficient (25—1000°C)	$18.77 \cdot 10^{-6}$
Specific electrical resistance (ohm · cm · 10^6) at:	
0°C	4.0
100°C	6.5
500°C	18.0
800°C	31.0
Electron work function, eV	3.92
Thermal neutron capture cross section, barns	0.0090

The existence of two crystalline modifications (close-packed hexagonal) at temperatures up to 1250 to 1260° and body-centered cubic at higher temperatures) was established only recently, because of the high allotropic transformation temperature (only 20 to 30° below the melting point).

The electrical conductivity of beryllium is 35 to 42% that of copper. Beryllium has a high penetrability for X-rays (16 to 17 times the penetrability of aluminum).

Beryllium has the highest heat of fusion of all metals. The heat capacity of beryllium increases sharply with increasing degree of purity. The thermal expansion coefficient at 25 to 100° is about half that of aluminum and magnesium.

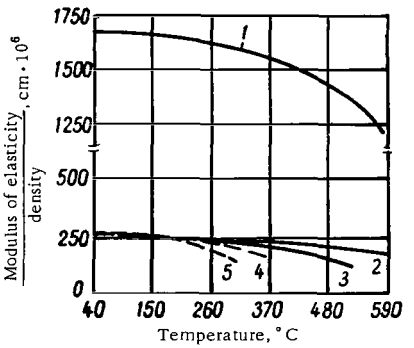

FIGURE 202. Modulus of elasticity-to-density ratio for beryllium and other structural metals at elevated temperatures.

1—beryllium; 2—stainless steel; 3—titanium (6 Al, 4 V); 4—aluminum (X2020); 5—magnesium (NK31A).

As compared with the other structural metals (including titanium) beryllium has a much higher specific strength which it retains up to 600 to 650° (Figure 202). However, it has the disadvantages of increased brittleness at room temperature and of strong anisotropy (different values of parameters measured in the longitudinal and in the perpendicular direction) of the properties of products made by pressure working. This is explained by the anisotropy hexagonal beryllium crystals, which become oriented in a given direction during pressure working. For instance, the tensile strength of extruded beryllium rods measured along the axis is 1.5 to 2 times that measured across the rod.

Obviously, no anisotropy is observed in beryllium products which have been prepared by casting or powder metallurgy and in which there is a random orientation of the crystals.

There are two views on the brittleness of beryllium: one attributed the brittleness to its atomic structure and the low value of the Poisson coefficient; the other attributes it to the presence in beryllium of soluble and insoluble contaminants. In the case of technically pure beryllium, a transition from the ductile to the brittle state takes place at about 200°. The transition temperature decreases as the degree of purity of the metal is increased. Beryllium produced by direct extrusion from the electrolytic powder (flakes) has superior strength characteristics as compared with the metal extruded from the cast metal (Table 65).

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The modulus of elasticity of technical beryllium is $\sim 28{,}000\,kg/mm^2$, the modulus of rigidity is $\sim 13{,}800\,kg/mm^2$. Depending on the degree of deformation and the holding time, the recrystallization temperature of beryllium ranges from 700 to 900°. The Brinell hardness of technical beryllium produced by different methods is 100 to $150\,kg/mm^2$.

The most important problem in the metallurgy of beryllium is the development of techniques for the production of a ductile metal. One of the ways in which this can be accomplished is by increasing the purity of the metal. While the elongation (under a tensile load) of technical beryllium is only 0.3 to 7%, the elongation of pure monocrystal beryllium reaches 70 to 80 and occasionally 140% (in creep deformation along the base plane of the hexagonal crystalline cell of beryllium it may be as high as 220%).

Beryllium has five known isotopes, of which only Be_4^9 is stable (the unstable isotopes are Be^6, Be^7, Be^8, Be^{10} and Be^{11}). Beryllium has a very low thermal neutron capture cross section — 0.009 barn.

TABLE 65

Mechanical properties of beryllium extruded at 1060° and annealed at 800°

Metal	Tensile strength, kg/mm^2	Elongation, %
Extruded from electrolytic powder..	41.5—54.8	4—7
Extruded from cast beryllium	25.3—38.7	1.5—4.0

The structure of the nucleus of a beryllium atom is characterized by its low neutron bond energy, which makes it possible to use beryllium as a neutron source. In addition, beryllium has the ability to scatter neutrons by changing their direction and reducing their energy.

Irradiation at temperatures up to 450° has very little effect on the mechanical, electrical, and corrosion properties of beryllium.

Noticeable oxidation of solid beryllium in air begins at 700° and proceeds rapidly at 1000°.

A reaction between beryllium and nitrogen begins at 725° (it is observed as an irridescent color), and the formation of beryllium nitride begins at 900° but the rate of formation remains very low even at 1100°. With ammonia, a much faster reaction is observed at the same and even at lower temperatures. Beryllium does not combine directly with hydrogen. The hydride $(BeH_2)x$ has been prepared by decomposition of organoberyllium compounds in the form of a solid solution which decomposes above 200°.

Finely dispersed beryllium reacts vigorously with sulfur, selenium, and tellurium vapors, yielding sulfides, selenides, and tellurides. Molten beryllium reacts with carbon forming the carbide Be_2C and under certain conditions BeC_2.

Beryllium dissolves in hydrochloric and sulfuric acid of any concentration, but is not dissolved by cold concentrated nitric acid. By analogy with aluminum, beryllium dissolves in concentrated or hot dilute solutions of alkalies, yielding beryllates (e.g., K_2BeO_2). In comparison with aluminum, beryllium is more resistant to the action of alkalies. Beryllium does not react with aqueous solutions of ammonium hydroxide. A rapid reaction between beryllium and the halogens takes place upon slight heating.

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The corrosion resistance of beryllium in water is strongly affected by the methods used for its preparation and processing and its chemical composition. Usually, beryllium has a higher resistance to corrosion in water of a higher alkalinity, e. g., ~ pH 8. A sharp increase in the corrosion rate is caused by the presence in the water of dissolved oxygen and Cl^-, SO_4^{2-}, Cu^{2+}, and Fe^{3+} ions.

Up to 600 to 800° beryllium has a satisfactory resistance to corrosion in contact with some molten metals and alloys (Bi, Bi—Pb, Bi—Pb—Sn, Na, K, Na—K, Pb).

The properties of beryllium compounds

Oxides. The only beryllium oxide known, BeO, is formed by burning the powdered metal in oxygen or in air, or by ignition of beryllium hydroxide, sulfate, carbonate or nitrate.

Beryllium oxide is characterized by a high refractoriness (mp 2550°, bp 4260°) and a strong chemical bonding (the heat of formation from the elements is 143 kcal/mole). BeO has a hexagonal crystalline lattice (of the wurtzite type) with the parameters: a = 2.69 Å, c = 4.39 Å, c/a = 1.62. The density of BeO is 3.03 g/cm^3. At temperatures up to 500° the heat conductivity of BeO is much higher than that of Al_2O_3 and MgO. BeO is a good electrical insulator up to 1000 to 1200°. It has a moderate thermal expansion coefficient ($10.8 \cdot 10^{-6}$ at 25 to 1000°).

The solubility of BeO in water is extremely small (0.002 to 0.008 mmoles BeO/liter H_2O). Freshly prepared BeO dissolves readily in acids, alkalies and ammonium carbonate with the formation of beryllium salts or alkali beryllates. However, a sharp decrease in the chemical activity of BeO occurs upon ignition at 1200 to 1500° (because of the large increase in the grain size), and the ignited BeO is soluble only in HF, molten cryolite (Na_3AlF_6) and molten potassium bisulfate ($KHSO_4$).

Beryllium oxide resists attack by molten lithium and potassium up to 800°, calcium up to 600° and gallium up to 1000°; there is almost no interaction between BeO and molten iron, nickel, molybdenum, thorium, cerium, and platinum. At 1800° BeO reacts with niobium, silicon, titanium, and zirconium. In contact with carbon, BeO is not attacked up to 1600 to 1800°.

Beryllium oxide is not reduced by hydrogen, sodium, potassium, magnesium, and aluminum upon heating to very high temperatures.

Beryllium hydroxide is precipitated from solutions of beryllium salts by solutions of alkali hydroxides and ammonium hydroxide, at pH 6 to 8, in the form of a white, amorphous, gelatinuous precipitate with the formula $Be(OH)_2 \cdot xH_2O$.

The solubility of $Be(OH)_2$ in ammonium hydroxide solutions is very low; the freshly precipitated hydroxide dissolves in alkalies yielding beryllates:

$$Be(OH)_2 + 2NaOH = Na_2BeO_2 + 2H_2O.$$

The alkali-metal beryllates are strongly hydrolyzed in water. In contrast to $Al(OH)_3$, beryllium hydroxide dissolves in a solution of ammonium carbonate, yielding the complex beryllium carbonate:

$$Be(OH)_2 + 2(NH_4)_2CO_3 = (NH_4)_2[Be(CO_3)_2] + 2NH_4OH.$$

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This property may be used for the separation of beryllium hydroxide from large amounts of aluminum.

The complex carbonate is hydrolyzed upon boiling, with the precipitation of a sparingly soluble basic salt of beryllium:

$$2(NH_4)_2[Be(CO_3)_2] + H_2O = Be(OH)_2 \cdot BeCO_3 \downarrow + 2(NH_4)_2CO_3 + CO_2.$$

There are three known modifications of beryllium hydroxide: an amorphous form, a metastable (α-) crystalline form, and a stable β-form. The amorphous form consists of the above-mentioned hydrate $Be(OH)_2 \cdot xH_2O$ (up to 95% water) precipitated from a cold solution. When stored in air or in water the hydroxide is aged and is converted into the metastable α-form; the β-form is precipitated from boiling solutions of the beryllates. Upon aging, beryllium hydroxide becomes insoluble in alkalies and even in acids.

Beryllium hydroxide loses most of its water when heated to 200 to 300°, but for quantitative dehydration heating to a high temperature (700 to 800°) is required.

Halides. Beryllium fluoride is produced by the reaction between fluorine and beryllium oxide, oxyfluoride or carbide, or by the decomposition of the complex ammonium fluoberyllate:

$$(NH_4)_2BeF_4 \rightarrow BeF_2 + 2NH_4F.$$

Beryllium fluoride is a colorless, very hygroscopic crystalline substance, with a mp of 787 and a bp of 1327°. Its density is 1.986 g/cm^3. Upon heating in oxygen or in air it is converted into the oxyfluoride $5BeF_2 \cdot 2BeO$; beryllium fluoride reacts with the alkali metal fluorides and ammonium fluoride yielding complex fluoberyllates (Na_2BeF_4, $NaBeF_3$).

In contrast to AlF_3, BeF_3 dissolves readily in water (its maximum concentration in the solution is 18 moles/l), a fact which may be used for the separation of aluminum and beryllium in the hydrometallurgical processing of raw materials.

Sodium tetrafluoberyllate Na_2BeF_4 is the most stable of the sodium beryllates; it is known to exist in three crystalline forms. The γ-form has a rhombohedral structure, it is stable at room temperature, and is the least water soluble form of Na_2BeF_4 (at 20° its solubility is 1.37 g/100 g solution). The β-form (which has a monoclinic structure) is very unstable and is readily converted into the γ-form. Its solubility in water at 20° is 1.7 g/100 g solution. The α-form (with a hexagonal structure) is formed above 300° and is converted into the γ-form upon cooling.

Ammonium tetrafluoberyllate $(NH_4)_2BeF_4$ is the most important of the ammonium fluoberyllates; its solubility at 0 and 25° is 27.1 and 32.3 g/100 g of solution respectively. Ammonium fluoberyllate forms mixed crystals with sulfates; upon heating to 900° it decomposes to ammonium fluoride and beryllium fluoride.

Beryllium chloride $BeCl_2$ is produced by heating the metal to 600° in a current of chlorine or by chlorination of a BeO + C mixture at 700 to 800°; it is a white crystalline substance with a mp of 405°. The chloride is volatilized at 477° and boils at 487°. The density of $BeCl_2$ is 1.9. It is readily soluble in water and crystallizes from aqueous solutions as the crystalline hydrate $BeCl_2 \cdot 2H_2O$. $BeCl_2$ hydrolyzes in humid air or in water with the evolution of hydrogen chloride:

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$$BeCl_2 + 2H_2O = Be(OH)_2 + 2HCl.$$

$BeCl_2$ readily dissolves in organic solvents (alcohol, ether, pyridine, acetone) and forms organometallic compounds.

Beryllium sulfate $BeSO_4$ is produced by dissolving beryllium oxide in hot concentrated sulfuric acid. $BeSO_4$ undergoes a polymorphic transformation at 580 to 635°, its thermal dissociation starts at 760 to 830° (with the evolution of SO_3), and total decomposition occurs at 1200 to 1300°.

Beryllium sulfate readily dissolves in water, and its solubility increases markedly with increasing temperature:

Temperature, °C	30	40	85	95.4	111
Solubility of $BeSO_4$, % by weight....	29.75	31.11	42.28	52.35	54.70

The sulfate crystallizes from aqueous solutions as the hydrate $BeSO_4 + 4H_2O$, and forms double salts (of the $MeSO_4 \cdot BeSO_4 \cdot xH_2O$ type) with the sulfates of the alkali metals, ammonium, copper, and zinc; the double salts are readily soluble in water.

Carbonates. Basic beryllium carbonates of variable composition ($BeCO_3 \cdot nBe(OH)_2 \cdot mH_2O$ where n = 2, 3, 4, 5, 7 and m = 1, 2, 3) are formed upon the addition of a solution of Na_2CO_3 or $(NH_4)_2CO_3$ to a solution of beryllium salts. The normal carbonate $BeCO_3 \cdot 4H_2O$ is formed only in the presence of a large excess of carbon dioxide in the solution.

Beryllium carbonate is readily hydrolyzed by water, yielding basic beryllium salts. The beryllium carbonates dissolve in an excess of ammonium carbonate and, with some difficulty, in an excess of sodium or potassium carbonate, yielding the double salts: $(NH_4)_2CO_3 \cdot BeCO_3$, $K_2CO_3 \cdot BeCO_3$, etc.

The basic beryllium acetate $Be_4O(CH_3COO)_6$ is formed by the reaction between acetic acid and beryllium hydroxide or carbonate. This salt has a mp of 284° and a bp of 331°. The distillation of the basic acetate is used as the basis of a process for the purification of beryllium (only zinc and zirconium have volatile acetates). The basic acetate is sparingly soluble in water but readily dissolves in chloroform.

Beryllium carbide Be_2C has a density of 2.3 to 2.4 and a cubic structure (of the CaF_2 type) with a lattice parameter a = 4.33 Å. Depending on the particle size, the color of the carbide ranges from yellow-red to gray-black. Be_2C is very hard, and its hardness exceeds that of silicon carbide (carborundun); it melts (with decomposition) at 2150°. In a vacuum, noticeable volatilization starts at 1600 to 1700° and at 2100° its vapor pressure reaches 1.5 mm Hg. Beryllium carbide is decomposed by water:

$$Be_2C + 4H_2O = 2Be(OH)_2 + CH_4.$$

At ~ 1000° the carbide reacts with nitrogen yielding beryllium nitride Be_3N_2. It is slowly oxidized by dry oxygen. It dissolves in dilute inorganic acids.

Beryllium carbide is produced by heating a mixture of beryllium and carbon to 1700° in vacuum or in an inert atmosphere, or by reduction of beryllium oxide with carbon at 1900°.

The chemical compounds of beryllium and metals are known as **beryllides.** Their most important properties are: resistance to oxidation at high temperatures (which in some cases may attain 1400°); high bending strength at elevated temperatures; brittleness at room temperature and, in some cases, the possibility of plastic deformation above 1200 to 1300°; high melting points (in the case of the beryllides

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of the rare refractory metals); great hardness. The beryllides of 40 elements are known at present, and the existence has been established of 90 binary beryllide phases and a large number of ternary and multi-component phases containing beryllium. The physical properties of some of the beryllides with the highest melting points are listed in Table 66.

There are several methods for the preparation of the beryllides: synthesis from the components, either by fusing together or by sintering the powders (powder metallurgy method) which is often carried out in vacuo and after which the sintered pellets are crushed and the resulting beryllide powders are converted into dense, solid products by hot pressing; metallothermic methods which involve the reduction of beryllium oxide with the metal whose beryllide is to be produced and which at the same time produces a volatile or low-melting oxide. It should be mentioned that because of the high vapor pressure of beryllium at elevated temperatures, beryllides of a predetermined composition may be produced mainly by powder metallurgy methods (which do not require a high temperature) while fusion and metallothermic methods are only seldom used.

TABLE 66

Properties of the beryllides of some metals

Beryllide	Melting point, °C	Density, g/cm³	Vickers hardness, kg/mm²	Modulus of elasticity at 1260°, kg/mm²	Bending strength at 1260°, kg/mm²	Weight increase after oxidation for 100 hrs at 1260°, mg/cm²
$TiBe_{12}$	>1430	2.26	—	—	7.8	3.0
$ZrBe_{13}$	1930	2.72	1000	44100	28.0	7.8
Zr_2Be_{17}	~1990	3.08	1130	18300	27.7	—
Hf_2Be_{17}	—	—	1085	12000	—	—
VBe_{12}	—	2.37	—	—	—	—
$NbBe_{12}$	1700	2.91	500	21100	31.5	1.7
Nb_2Be_{17}	>1700	3.28	1000	15500	49.1	2.6
Ta_2Be_{12}	1850	4.18	720	16900	37.4	18.0
$TaBe_{17}$	1980	5.05	1120	12000	54.7	—
$CrBe_2$	1840	4.34	1288	—	—	2.4
$MoBe_2$	1840	6.12	—	—	—	—
$MoBe_{12}$	~1700	3.02	950	10500	—	2.6

The beryllides are metal-like compounds which are attractive as refractory materials, components of refractory alloys, and as materials with special nuclear-physical properties. Some beryllides have semiconductor properties and are of interest for high-temperature semiconductor technology and also in industrial catalytic processes. Many refractory metals can be effectively protected against corrosion at high temperatures by creating on their surface a refractory coating composed of the beryllide of the respective metal.

Uses of beryllium /2—5, 11/

The consumption of beryllium is constantly increasing, because of the valuable properties of metallic beryllium and beryllium compounds and alloys. In the USA the consumption of beryllium was almost tripled between 1954 and 1958.

Most of the beryllium is consumed in the new branches of technology, e. g., the nuclear and missile industries and in the production of various alloys.

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Nuclear technology. The small mass of the beryllium atom* together with the small thermal neutron capture cross section combine to make beryllium an effective material for the moderation of neutrons to the velocities at which a chain reaction in a nuclear reactor has the highest productivity. As a neutron-moderating material, beryllium is superior to hydrogen, deuterium, graphite, and oxygen. Moreover, beryllium reflects neutrons and may be used for the manufacturing of reflectors for nuclear reactors (the use of such reflectors for the shielding of the active zone, i.e., the zone containing the nuclear fuel, makes it possible to reduce the dimensions of that zone). The use of beryllium as a moderator, reflector and structural material in reactors is also favored by the fact that it resists the effect of neutron bombardment (does not change its dimensions and properties), by the absence of noticeable induced radiation, and by its high thermal conductivity. The use of beryllium as a light metal is especially convenient for the nuclear reactors of transportation vessels (boats, including submarines, airplanes, etc.).

The use of beryllium as a shell for reactor fuel elements makes it possible to increase the shell temperature to 500 to 600°. The fact that beryllium emits neutrons upon bombardment with α-particles is used for the production of radium-beryllium and polonium-beryllium neutron sources. Beryllium foil is used as the window in Geiger counters, scintillation counters, etc.

In addition to beryllium, the less expensive beryllium oxide and beryllium carbide also find use in nuclear technology.

Jet aircraft and missile technology. Beryllium has a high specific modulus of elasticity up to 600 to 700° (see Figure 202). As a result, beryllium has a promising use as a lining for the fairings in supersonic jet aircraft, the nose cones of rockets and guided missiles, etc.

The high heat of combustion of beryllium and some beryllium compounds favor their use as components of solid missile fuels. Thus, the heat of combustion of beryllium borohydride $Be(BH_4)_2$ is 16100 kcal/kg, i.e., the highest of all boron and beryllium compounds. The heat of combustion of beryllium metal is also high, i.e., 15,000 kcal/kg.

Production of alloys. The most important industrial use of beryllium as yet is the production of dispersion-hardening alloys, mainly copper-based ones (beryllium bronzes, containing 0.5 to 3.0% Be).

The capacity for aging (dispersion hardening) is associated with the formation of hard and sufficiently high-melting solid compounds (beryllides) between beryllium and almost all other metals; during the aging, the beryllides are precipitated in a finely-divided form on the grain boundaries of the main alloy.

The addition of beryllium to copper improves its mechanical properties (hardness to 400 kg/mm^2, the tensile strength to 120 to 130 kg/mm^2, the fatigue limit upon bending to 30 to 32 kg/mm^2, and the fatigue limit upon torsion to 17 to 19 kg/mm^2). The high strength characteristics of beryllium bronzes are the reason for their extensive use in the production of critical machine parts (springs, valve seats, valves, bearings, various

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* In the case of neutrons the loss of energy (i.e., the decrease in velocity) upon collision with a nucleus increases as the mass of the nucleus approaches that of the neutron, by analogy with the case of two colliding billiard balls, in which the loss of energy is greatest when the two balls have the same masses.

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instrument parts, watch mechanisms, telephone and telegraph parts). The absence of spark upon impact makes it possible to use beryllium bronzes for the production of sparkless work tools (chisels, hammers, etc.) for use in mines, in handling flammable materials, and in plants with incendiary hazards. In addition, beryllium bronzes have a high corrosion resistance to heating in air and to sea water. Beryllium is added to copper as a copper-beryllium master alloy containing ~ 4% Be.

Beryllium finds an extensive use as an alloying component in steels and aluminum, magnesium, nickel, and chromium alloys. Of the more important beryllium-containing aluminum alloys we may mention the brands AMg6 (an Al—Mg alloy containing 0.0001 to 0.005% Be), and AL8U (0.05 to 0.15% Be) which retain their strength and ductility up to 250 to 300° and at the same time have an improved corrosion resistance.

Beryllium is a good deoxidant in the smelting of various alloys, including light alloys, bronzes, and aluminum alloys.

The addition of beryllium to magnesium and magnesium-based alloys makes it possible to reduce the waste of material during the smelting and casting, to reduce the hydrogen consumption and at the same time to eliminate the porosity of cast products.

The addition of beryllium to iron increases its coercive force.

The addition of beryllium to iron-nickel and iron-chromium alloys makes the structure of the alloy finer and, in addition to being very hard, the alloys also become fairly ductile and corrosion-resistant. Chromium-nickel steels containing beryllium are of improved refractoriness. Beryllium is usually added to iron and steel in the form of ferroberyllium (up to 80% Be).

Great prospects for the use of beryllium alloys are offered by the existence of the high-temperature β-modification of beryllium, which has a body-centered cubic lattice and thus is more ductile than the hexagonal α-form. It is of importance to stabilize the β-modification by alloying the beryllium with other metals and especially with nickel, chromium, cobalt, copper, manganese, and iron. Nickel is a good stabilizer of the β-modification; the addition of nickel (8%) to beryllium makes the beryllium ductile up to 1070° while technical beryllium containing no nickel is destroyed at that temperature.

The manufacturing of refractories. Because of its high melting point, strength, high thermal conductivity, high electrical resistivity, and resistance to heating, beryllium oxide has become an important component of high-quality refractories. Beryllium oxide is used for the manufacturing of crucibles, tubes, linings for coreless induction furnaces, and shielding for graphite crucibles (to reduce losses through radiation).

Missile bodies may be coated with a layer of beryllium oxide. This coating is vaporized during the passage of the missile through the dense layers of the atmosphere, and the vaporization consumes a large amount of heat. Of the other fields in which beryllium and beryllium compounds are used, we should mention X-ray technology (windows in X-ray tubes), electronics, and catalysis.

105. BERYLLIUM MINERALS AND ORES

The average concentration of beryllium in the Earth's crust is $6 \cdot 10^{-4}$%. There are more than 30 known beryllium minerals; of these, the most

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common are beryl, chrysoberyl, phenacite, helvite, danalite, and bertrandite. Beryl is the main commercial beryllium mineral, but phenacite and helvite are also of commercial value.

Beryl $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ [or $Be_3Al_2(Si_6O_{12})$] contains 14.1% BeO, 19.0% Al_2O_3, and 66.9% SiO_2. It is often contaminated with Na_2O, Li_2O, K_2O, Rb_2O and Cs_2O. Depending on the nature of the impurities they contain, beryls are classified as alkali-free (total alkali content below 0.5%) and alkaline beryls (total alkali content above 0.5%). The alkali-free group comprises the previous-stone beryls — the blue aquamarine, the wine-yellow heliodor (colored by iron), and the green emerald (colored by chromium).

The Mohs hardness of beryl is 7.5 to 8, its density is 2.63 to 2.91.

Phenacite or beryllium silicate $2BeO \cdot SiO_2$ [or $Be_2(SiO_4)$] contains 45.5% BeO, 54.5% SiO_2, and very small amounts of MgO, CaO, Al_2O_3, and Na_2O. Phenacite is either colorless or light yellow. Its Mohs hardness is 7.5, its density is 2.96 to 3.0. It is often associated with beryl, chrysoberyl, and felspars; it is very often found in emeralds. Phenacite forms no concentrated deposits.

Helvite $Mn_8(BeSiO_4)_6S_2$ contains 13.6% BeO and (in the form of impurities) up to 15% Fe, Zn, etc. Its color is most often yellow and more rarely green; its Mohs hardness is 6 to 6.5, and its density is 3.16 to 3.36.

Outside the USSR, the main beryllium ore deposits are found in Brazil, Argentina, Congo (Leopoldville), India, Southern Rhodesia, Australia, and the USA (South Dakota and California). All these deposits contain mostly beryl. The largest phenacite and helvite deposits are in Norway.

The production of beryllium concentrates in the Western countries increased continuously after the Second World War, up to 1956. The maximum production level — 11,700 tons of concentrate (11 to 13% BeO) — was reached in 1956.

According to approximate data, the world production of beryllium concentrates was 8100 tons in 1960.

106. ENRICHMENT OF BERYLLIUM ORES

The beryllium ores are usually of a low beryllium content; in most ores the BeO concentration ranges from 0.2 to 2%.

The enrichment of beryllium ores is quite difficult, because of the similar properties of the minerals (especially beryl) and the barren rock.

As yet, the main method for the extraction of beryllium from the ores consists of sorting large and medium beryl crystals. It is based on the difference in color between the beryl crystals and the accompanying minerals. Pure beryl crystals 5 to 10 mm in size are picked by hand. A recently developed automatic radiometric sorting method is based on the utilization of the radioactivity induced in the mineral by γ-irradiation or neutron bombardment.

Finely impregnated beryl ores may be effectively enriched only by flotation methods, which are being intensively developed. The beryl is floated with fatty acids (of these oleic acid is the one most thoroughly studied); there are two flotation schemes (acid and alkaline) which are different in principle. Sulfuric and hydrofluoric acids are used as

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regulators in acid flotation, while sodium sulfide, sodium hydroxide or sodium carbonate are used in alkaline flotation. The flotation of beryl with cationic collectors is also possible.

The approximate chemical composition of beryl concentrates is as follows:

BeO	10—13
SiO_2	62—65
Al_2O_3	17—23
Fe_2O_3	0.4—2.0
CaO	0.3—3.0
MgO	0—0.7
Li_2O	0—0.8
K_2O	0—0.2
Na_2O	0—1.5

107. METHODS OF PROCESSING BERYL CONCENTRATES

Beryl concentrates are in most cases processed to beryllium oxide, which is then converted to the anhydrous beryllium chloride or fluoride — the main starting materials for the production of beryllium by electrolysis — or are processed by thermal reduction with magnesium.

Two industrial methods for the decomposition of beryl are used at present: the fluoride method and the sulfate method. In the fluoride process the concentrate is sintered with sodium fluosilicate, yielding sodium fluoberyllate which is then treated with an alkali hydroxide to yield beryllium hydroxide which is then ignited to beryllium oxide. The sulfate process consists of a preliminary fusion and granulation of the beryl or sintering with lime, followed by sulfatizing, leaching with water, removal of impurities (Al, Fe, Mn) from the sulfate solution, and crystallization of beryllium sulfate or precipitation of beryllium hydroxide which are then roasted to beryllium oxide.

The most common method for the purification of beryllium and its isolation from sulfate solutions is based on the fact that, in contrast to aluminum, beryllium forms no alums, and on the low solubility of the aluminum-ammonium alums in the beryllium sulfate-ammonium sulfate solution.

The dependence of the solubilities of $Al_2(SO_4)_3$, $BeSO_4$ and $MgSO_4$ on the concentration of ammonium sulfate in the solution is shown in Figure 203. While the aluminum-ammonium alums have a low solubility (5 to 8 g/l) in solutions containing $\geqslant 100$ g/l $(NH_4)_2SO_4$, the solubility of beryllium sulfate is 300 g/l in solutions containing up to 250 g/l $(NH_4)_2SO_4$. The behavior of magnesium sulfate (beryl concentrates are often contaminated with magnesium) resembles that of aluminum, i. e., its solubility in solutions containing ammonium sulfate is very low. In addition, beryllium can be precipitated from a solution by the hydrolytic method, which is based on the fact that solutions of alkali beryllates are hydrolyzed upon boiling, with the precipitation of beryllium hydroxide. Beryllium compounds of a higher degree of purity are obtained by the precipitation of the sparingly soluble double beryllium potassium oxalate ($2BeC_2O_4 \cdot 2K_2C_2O_4$), which is formed when a beryllium-containing solution is treated with a solution of potassium oxalate.

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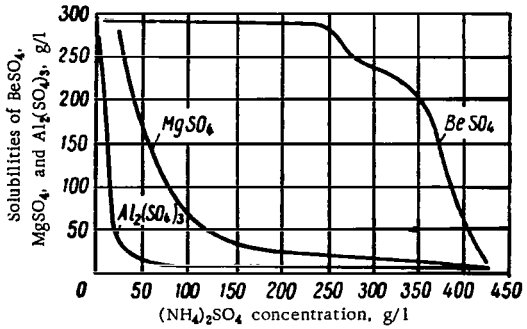

FIGURE 203. Dependence of the solubilities of $Al_2(SO_4)_3$, $BeSO_4$, and $MgSO_4$ on the ammonium sulfate concentration in the solution.

The sulfate process

The flow sheet of one of the technological processes for the processing of beryl concentrates by the sulfate method (including the advance sintering of the concentrate with lime) is shown in Figure 204.

Sintering (fusion). The concentrate is mixed with lime (at a ratio of 2 : 1) and fused in carbon-lined electrical furnaces at 1500 to 1600° or sintered in rotary kilns. The fusion is to be preferred since for sintering the mixture components must be crushed to a fine particle size and mixed more thoroughly than in the case of the fusion; however, even after such crushing and mixing, the rate and degree of completion of the sintering are inferior to those obtained in the fusion. The beryl is decomposed during the sintering or fusion, yielding complex beryllium silicates (which are treated with relative ease with sulfuric acid) and calcium silicate:

$$3BeO \cdot Al_2O_3 \cdot 6SiO_2 + CaO \rightarrow 3BeO \cdot Al_2O_3 \cdot 6CaSiO_3$$

Sulfatizing. The fused mass from the electrical furnace or the sintered mass from the rotary kiln are granulated in water (yielding brittle granules of the so-called beryl glass) and ground in a ball mill to a particle size of 0.1 to 0.074 mm. The ground material is taken for sulfatizing, i.e., treatment with sulfuric acid (in a 10% excess above the stoichiometric amount required for the formation of aluminum, magnesium, and beryllium sulfates). The sulfatizing is carried out with concentrated sulfuric acid in a steel reactor or with 63% sulfuric acid in an autoclave (in addition to the acid, water is added in order to heat the reaction mass).

Leaching. The aluminum, beryllium, magnesium, and calcium sulfates formed in the treatment with sulfuric acid are leached with hot wash waters (from the preceding cycles) in rotary horizontal leachers or reactors fitted with stirrers. Subsequent filtration and washing of the solid residue (consisting of calcium sulfate and silica) yield sulfate solutions containing 32 g/l BeO, 35 g/l Al_2O_3, and 2 to 3 g/l Fe_2O_3.

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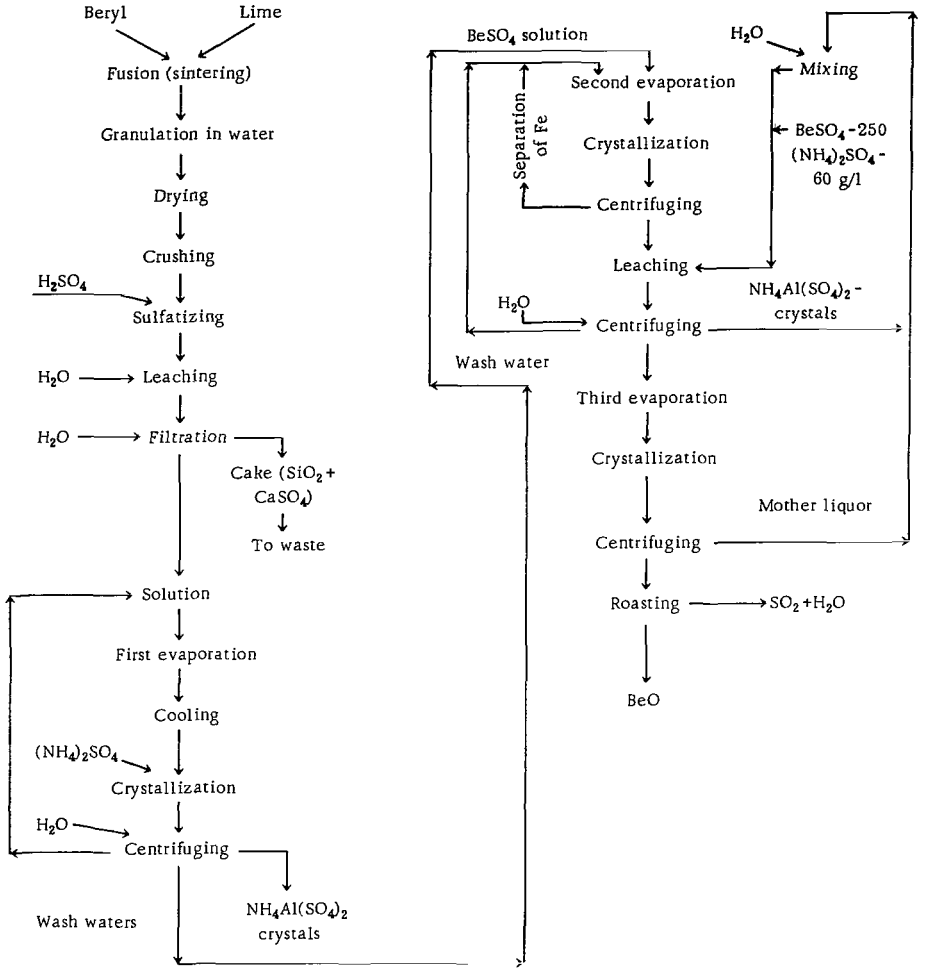

FIGURE 204. Flow sheet of the production of beryllium oxide by the sulfate process with preliminary sintering of the concentrate with lime.

Evaporation and crystallization. The solution is evaporated to a density of 1.32, transferred to a crystallizer, and there treated with $(NH_4)_2SO_4$ (in 25% excess over the stoichiometric amount needed for the crystallization) thus causing precipitation of alum $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. In order to isolate the alum the solution is cooled to 15°, the alum is allowed to crystallize, and the mother liquor is evaporated to precipitate the residual alum and the bulk of the beryllium sulfate. The precipitate is then treated with a solution containing $BeSO_4$ (250 g/l) and $(NH_4)_2SO_4$ (60 g/l). As a result of the leaching the bulk of the $BeSO_4$ is extracted yielding a solution free of aluminum and containing 750 g/l $BeSO_4$. Tetrahydrates ($BeSO_4 \cdot 4H_2O$) are isolated by evaporation of the above

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solution and crystallization. The iron sulfate is separated from the mother liquor from the second crystallization (which contains ammonium and iron sulfates and some $BeSO_4$) and the solution is combined with the solution used for the second crystallization.

The concentration of calcium sulfate in the solution containing aluminum and beryllium sulfates is determined by its solubility, which at 20° is 2 g/l; the solubility decreases during the evaporation and the $CaSO_4$ almost quantitatively passes into the solid phase during the precipitation of the alum.

Drying and roasting. The $BeSO_4 \cdot 4H_2O$ crystals are separated by centrifuging and roasted to yield beryllium oxide:

$$BeSO_4 \cdot 4H_2O = BeO + SO_3 + 4H_2O.$$

The roasting is carried out in a tubular rotary furnace at 1000 to 1150°; the product is beryllium oxide containing up to 0.1% $Fe_2O_3 + Al_2O_3$, 0.08% CaO, and 0.2% SiO_2.

One of the widely used sulfate methods is based on the decomposition with sulfuric acid without a preliminary use of an alkaline flux during the fusion, which reduces the consumption of sulfuric acid. The beryl concentrate is fused without a flux and granulated in cold water, yielding a vitreous mass that is soluble in sulfuric acid.

In this case the fusion is carried out in an arc furnace at 1700°, the fused mass is granulated in rapidly running water, and the granulated mass is heated in a rotary gas furnace to 900° (in order to increase the degree of decomposition of the concentrate by the sulfuric acid). This makes it possible to convert 90% of the beryllium to a soluble form. The heat-treated fused mass is crushed in a ball mill to a particle size of -0.074 mm, subjected to air classification, and the further processing is in principle the same as that used in the first variant described above (Figure 205). There is a difference in that after the separation of the aluminum in the form of alum, beryllium hydroxide is precipitated from the sulfate solution by hydrolysis. For this purpose, sodium hydroxide is added to the solution (to a NaOH concentration of 1.5 N) and the solution is boiled. This causes hydrolysis of the sodium beryllate:

$$Na_2BeO_2 + 2H_2O \rightarrow Be(OH)_2 + 2NaOH.$$

A complexant such as EDTA (ethylenediamine tetraacetic acid) is added to the solution in order to retain the ions of some of the contaminants in solution. The hydroxide precipitate is dissolved in sulfuric acid and beryllium sulfate is then precipitated from the solution.

Decomposition of beryl concentrate by sintering with sodium fluosilicate (the fluoride process)

The sintering of beryl concentrate with sodium fluosilicate (which is a by-product of the processing of apatite to fertilizers) involves the reaction

$$3BeO \cdot Al_2O_3 \cdot 6SiO_2 + 6Na_2SiF_6 = 3Na_2BeF_4 + 2Na_3AlF_6 + 9SiO_2 + 3SiF_4.$$

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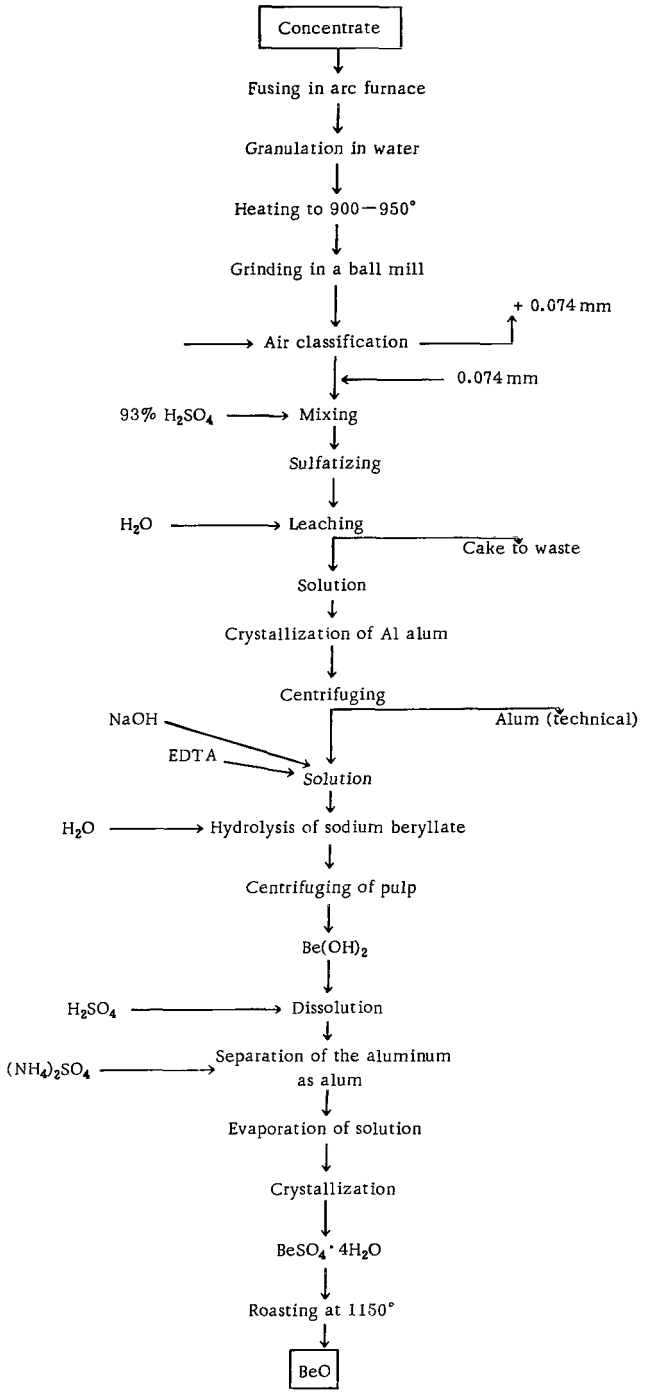

FIGURE 205. Flow sheet of the production of beryllium oxide by the sulfate method.

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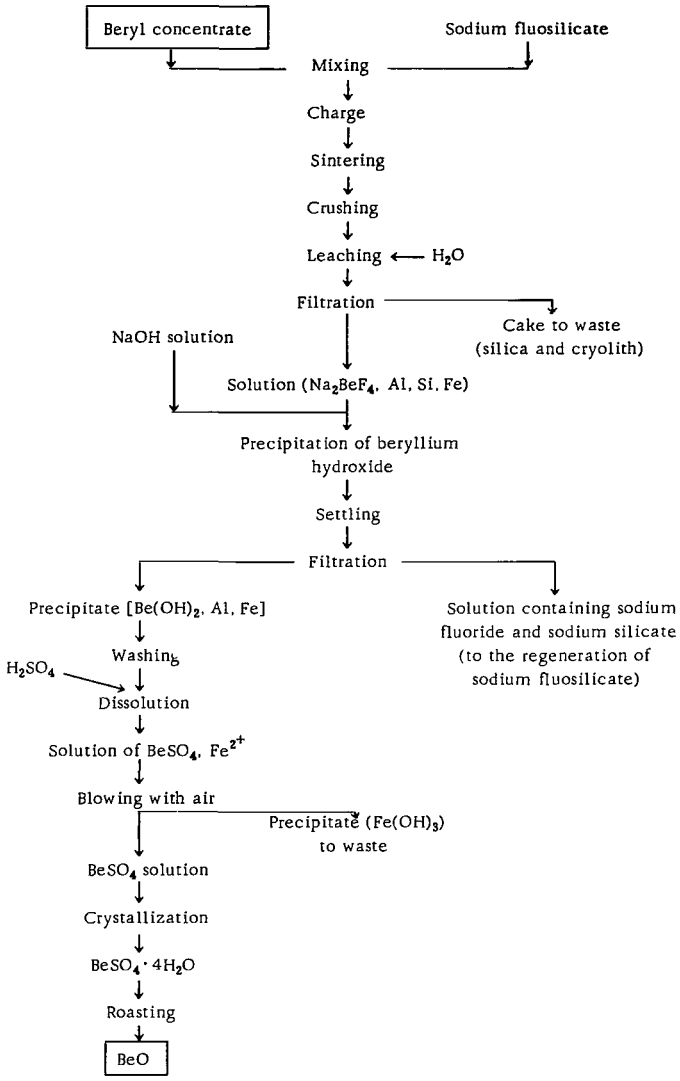

FIGURE 206. Flow sheet of the processing of beryl concentrate by sintering with sodium fluosilicate.

Since sodium fluoberyllate is the only water-soluble substance among the reaction products, it is easily leached, yielding fairly pure solutions.

The beryl concentrate (Figure 206) is crushed to a particle size of -0.1 mm and mixed in a drum with sodium fluosilicate, in a ratio of 1 : 1. The charge is sintered in rotary or muffle furnaces at 700 to 750° (the sintering in a rotary furnace is more advantageous since the thermal

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conductivity of the charge is low and the thickness of the layer in a muffle furnace must not exceed 25 mm). The sintered mass is crushed and leached with water, while heating with superheated steam; as a result the Na_2BeF_4 and a fraction of the aluminum, silicon and iron pass into the solution while the bulk of the aluminum and the silicon remain in the solid phase. The solid and liquid phases are separated in a filter-press and the cake is discarded. The composition of the salts dissolved in the solution is (converted to the oxides) 82 to 88% BeO, 6% Al_2O_3, 6 to 10% SiO_2 and a small amount of iron. The solution is heated with steam to 40 to 50° and beryllium hydroxide is precipitated by the addition of a 20% solution of sodium hydroxide:

$$Na_2BeF_4 + 2NaOH = Be(OH)_2 + 4NaF.$$

The addition of an excess of sodium hydroxide is to be avoided in order to prevent the conversion of the beryllium to soluble beryllates.

The hydroxide precipitate is allowed to settle for 2 to 3 hours, and is then separated by filtration in vacuum filters and washed with heating (with spent steam) to 70 to 80°. After the washing, the beryllium hydroxide precipitate is dissolved in sulfuric acid. Iron is removed from the solution by precipitation as the hydroxide or as a basic salt. The sulfate ($BeSO_4 \cdot 4H_2O$) is crystallized from the purified solution, and is then roasted to convert it into the oxide (as described above).

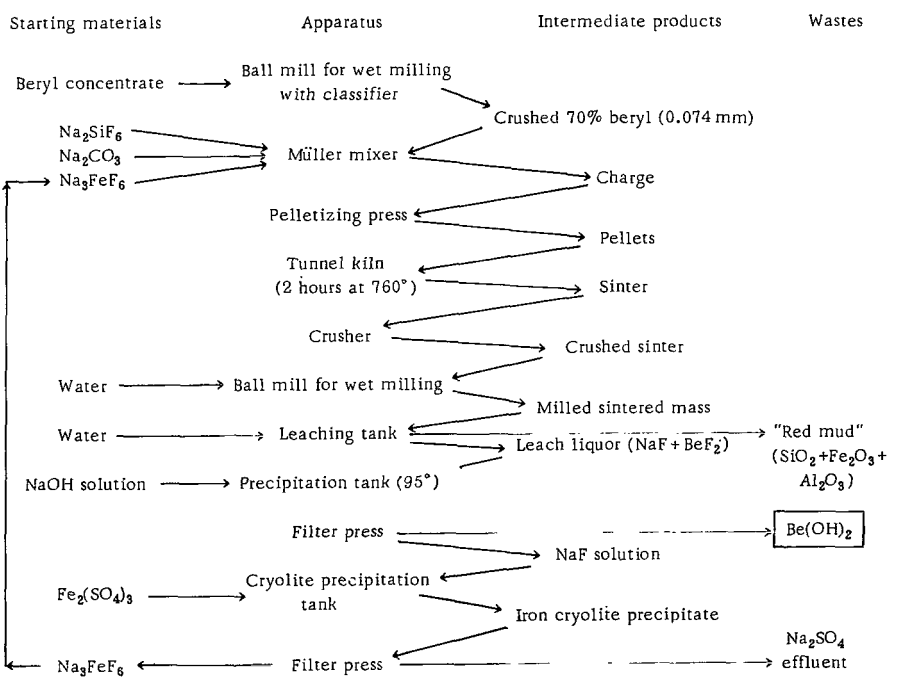

FIGURE 207. Flow sheet for the processing of beryl concentrate by sintering with sodium fluosilicate and iron cryolite.

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The decomposition of beryl with the aid of sodium fluosilicate has several variants. A variant extensively used in industrial practice involves the substitution of sodium carbonate and "iron cryolite" Na_3FeF_6 for part of the sodium fluosilicate in the charge:

$$3BeO \cdot Al_2O_3 \cdot 6SiO_2 + 2Na_2SiF_6 + Na_2CO_3 \rightarrow 3Na_2BeF_4 + 8SiO_2 + Al_2O_3 + CO_2,$$
$$3BeO \cdot Al_2O_3 \cdot 6SiO_2 + 2Na_3FeF_6 \rightarrow 3Na_2BeF_4 + Al_2O_3 + Fe_2O_3 + 6SiO_2.$$

This causes a sharp reduction in the consumption of the costly fluosilicate, since the sodium fluoride solution is returned to the formation of iron cryolite:

$$12NaF + Fe_2(SO_4)_3 = 2Na_3FeF_6 + 3Na_2SO_4.$$

A flow sheet of this variant as used in a plant belonging to the "Beryllium Corporation of America" is shown in Figure 207.

In this process, iron cryolite is used as a substitute for about 60% of the sodium fluosilicate; when the stoichiometric amount of reagents is consumed, about 92% of the beryllium originally present in the concentrate is converted to the soluble form, and the total degree of extraction of beryllium from the concentrate is 85 to 90%.

The concentrate is crushed, ground in a wet ball mill to a particle size of -0.074 mm, and mixed with moist sodium iron fluoride, sodium fluosilicate, and sodium carbonate (taken in a certain excess above the stoichiometric amount needed). The mixture is pelletized and sintered for 2 hours at 750° (in a tunnel kiln), the sintered pellets are crushed, ground in a ball mill, and the product is leached at room temperature. The precipitate is allowed to settle, the clear solution is separated by decantation, and beryllium hydroxide is then precipitated from the solution. To achieve the precipitation, the required amount of sodium hydroxide and a fraction of the solution (20% by volume) are transferred to an agitator (fitted with a stirrer and heated with superheated steam), heated to 95°, and the rest of the solution is added. The coarse-grained β-form is obtained by maintaining the pH at 12.

The beryllium hydroxide is separated by filtration, washed to remove sodium fluoride, and roasted in a rotary furnace at 1000° to yield beryllium oxide.

Production of beryllium chloride from beryllium oxide /2-6, 17-19/

The first to study the chlorination of beryllium oxide was Avdeev, in the middle of the nineteenth century. Many studies of the process were carried out by Soviet scientists — Spitsin, Belyaev, and Novoselova.

The chlorination of beryllium oxide with gaseous chlorine is usually carried out in the presence of carbon:

$$BeO + C + Cl_2 \rightarrow BeCl_2 + CO.$$

The reaction begins at 600° but the industrially favorable chlorination temperature is 900 to 950°. The chlorination temperature may be reduced sharply by using carbon tetrachloride as the chlorination agent:

$$2BeO + CCl_4 \rightarrow 2BeCl_2 + CO_2.$$

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This eliminates one operation — mixing of beryllium oxide with the carbon — and markedly simplifies the technological process. When CCl_4 is used, the chlorination of BeO may be carried out to a high degree of completion (92 to 94%) at 650 to 700°. A fraction of the CCl_4 is converted to C_2Cl_6 through thermal dissociation.

The chlorination rate of BeO is affected by the conditions of roasting (of beryllium hydroxide to BeO) before the chlorination, since the activity of beryllium oxide is reduced by high roasting temperatures.

The iron, aluminum, and silicon oxides present in the beryllium oxide as impurities are also chlorinated at the BeO chlorination temperature (900 to 950°) and pass (as the chlorides) into the gaseous phase together with $BeCl_2$.

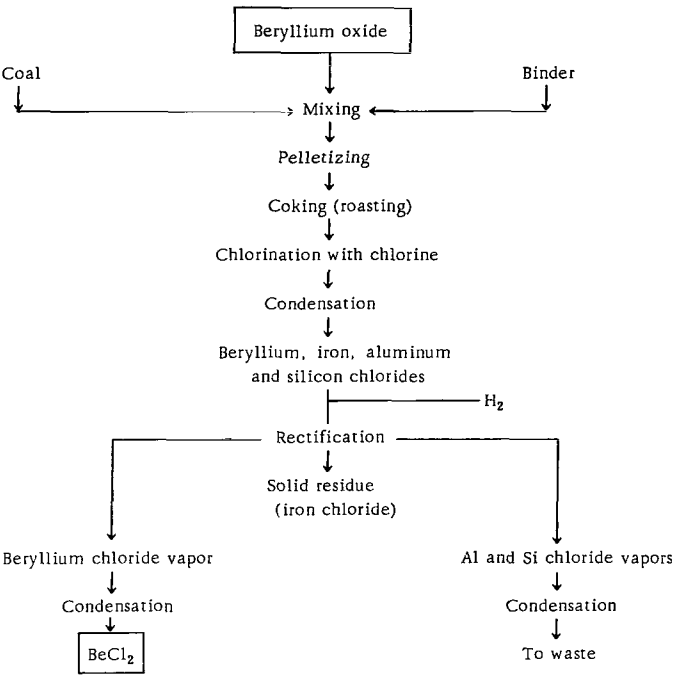

FIGURE 208. Flow sheet of the chlorination of beryllium oxide by chlorine.

Upon cooling the chloride mixture, beryllium chloride condenses first, followed by the iron, aluminum, and silicon chlorides in the order of their boiling points:

Chloride	$BeCl_2$	$FeCl_3$	Al_2Cl_6	$SiCl_4$
Boiling point, °C	492	319	183	58

However, the condensation does not result in a satisfactory purification of the beryllium chloride, and it is subsequently purified by a second distillation.

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Chlorination of beryllium oxide by chlorine in the presence of carbon (Figure 208). Dry beryllium hydroxide (50% BeO) is mixed with charcoal and a binder and is pelletized in a press under a pressure of 150 kg/cm^2 (see Figure 55). The pellets are coked at 1000° and then chlorinated in an electrical shaft furnace. Beryllium chloride is condensed in a bin-shaped nickel condenser. The beryllium chloride obtained by condensation is contaminated with iron, aluminum, and silicon chlorides and is purified by distillation in a current of H_2 in a steel muffle at 500 to 550°. As a result ferric chloride is converted to ferrous chloride which is not volatile at that temperature; the remaining chlorides enter two nickel collectors (placed one over the other) and beryllium chloride (97% of the total amount of $BeCl_2$) condenses in the first collector (which is heated to 350°) while the aluminum and silicon chlorides as well as 3% of the beryllium chloride condense in the second, unheated collector.

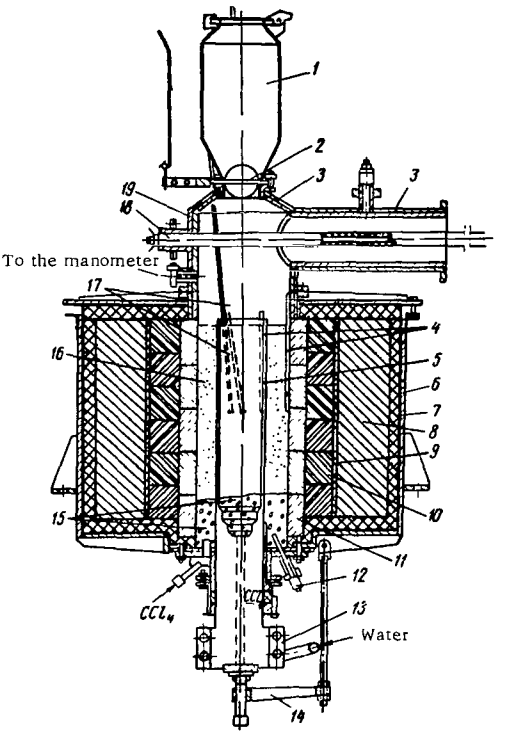

FIGURE 209. Diagram of a commercial furnace for the chlorination of beryllium oxide by carbon tetrachloride.

1—bin; 2—baffle plate; 3—graphite lining; 4—thermocouples; 5—graphite heater; 6—furnace jacket; 7—diabase tile; 8—chamotte foam bricks; 9—diabase plaster; 10—Dinas bricks; 11—quartz bricks; 12—thermocouple; 13—contact; 14—fastening device; 15—crushed quartz; 16—pelletized charge; 17—bars; 18—neck heater; 19—cap with tube connection.

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Chlorination of beryllium oxide by carbon tetrachloride is carried out in a furnace (Figure 209) consisting of a graphite heater in a shaft lined with fused quartz bricks. The carbon tetrachloride passes from a measuring vessel into the ring-shaped space between the heater and the furnace lining. The furnace lid is fitted with a cap with a tube connection and a charging bin made of stainless steel and lined with graphite. A nichrome heater protected by a quartz casing is fitted within the cap, to prevent condensation of the beryllium chloride.

The furnace is preheated in a current of nitrogen to the required temperature, and the feed of CCl_4 begun (the CCl_4 consumption is 2.4 kg/minute per square meter of furnace cross section). A new batch of beryllium oxide pellets is fed to the furnace every 6 hours; the pellets are prepared by pressing a mixture of BeO and a binder (a starch paste of dextrine), followed by drying at 200° and roasting in stainless-steel vessels at 600°. The total duration of a furnace run is determined by the service life of the graphite heater and ranges from 25 to 30 days.

The chlorination products pass into a condenser system: first into a nickel condenser heated to 300 to 320°, then into a second nickel condenser heated to 200 to 250° and then into a third unheated condenser made of IX18H9T stainless steel, which serves to condense the excess CCl_4, hexachloroethane (which distills off at 185.6°), the contaminant chlorides ($FeCl_3$, $AlCl_3$), and a small amount of entrained $BeCl_2$. The condensation product from the third condenser is treated on a filter with CCl_4, the resulting solution of hexachloroethane in CCl_4 is returned to the chlorination process, and the chlorides residue is returned to the hydrometallurgical processing in order to extract the beryllium.

The main technological and economical parameters of the process are as follows: CCl_4 consumption is 1.6 kg/kg $BeCl_2$, degree of condensation of $BeCl_2$ is 97.8%, the direct yield of beryllium is 85 to 86%, and the total yield (including the processing of wastes) is 96%.

108. PRODUCTION OF METALLIC BERYLLIUM

At present, beryllium is produced by thermal reduction of beryllium fluoride with magnesium or by electrolysis of beryllium chloride in molten salts.

Electrolysis of beryllium chloride

The electrolysis is carried out in a molten mixture of beryllium chloride and sodium chloride at a temperature below the melting point of metallic beryllium. The $BeCl_2$: NaCl ratio in the mixture is 1 : 1 by weight. This ratio is close to the eutectic composition (58.7 $BeCl_2$ + 41.3% NaCl) which melts at 215°. According to Delimarskii and Skobets, the decomposition potential of $BeCl_2$ in the molten eutectic mixture changes as a function of the temperature as follows:

Temperature, °C	420	600	700
Decomposition potential, V	2.08	1.99	1.93

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The electrolysis is carried out in a nickel crucible (500 mm in diameter and 800 mm high, with a nickel lid) which is heated by electrical current with the aid of an external resistance winding. The crucible serves as the cathode, and a graphite electrode, 100 mm in diameter and 1200 mm long, serves as the anode (Figure 210). The electrolyte temperature is 350°, the voltage (which is applied simultaneously to 10 electrolyzers) is 40 to 50 V, and the current is 500 amp.

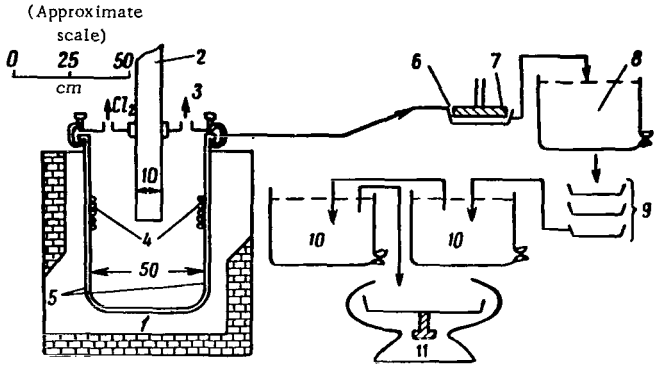

FIGURE 210. Diagram of the equipment used in the production of beryllium by electrolysis of beryllium chloride.

1—electrolyzer made of nickel sheets 2—3 mm thick; 2—anode; 3—opening in the crucible lid for the siphoning of the electrolyte into other electrolyzers; 4—metallic beryllium flakes on the walls; 5—external resistance winding for heating the electrolyzer; 6—gas-heated perforated ladle; 7—press for the separation of the electrolyte entrained from the bath from the metal flakes; 8—earthenware vessel for the washing of beryllium flakes; 9—washing screens arranged in cascade, for the removal of the last traces of beryllium chloride; 10—ceramic vessels for the removal (by washing) of beryllium oxide and aluminum oxide films from the beryllium flakes; 11—centrifuge for the final washing and drying of the beryllium flakes.

The chlorine evolved during the electrolysis is evacuated through an opening in the lid of the crucible. After an electrolysis time of 24 hours, the electrolyte is heated to 500° (to reduce its viscosity) and transferred by a nickel siphon into a series of other electrolyzers in which it is mixed with fresh batches of beryllium chloride and the electrolysis is continued.

The metallic beryllium, which is deposited as flakes on the crucible walls, is taken out while still hot and the electrolyte is removed by squeezing in a gas-heated press. The metal is allowed to cool, beryllium chloride is washed out with cold water, aluminum oxide is washed out with an alkali solution, and beryllium oxide is washed out with dilute nitric acid. The current efficiency is 60 to 65%. The beryllium concentration in the flakes is about 99%. The beryllium flakes are pressed into pellets (40 × 40 mm) in a hydraulic press under 5 tons/cm^2 and the pellets are fused (in order to yield solid beryllium) in beryllium oxide crucibles in a beryllium furnace with molybdenum heaters. The fusion is carried

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out at 1400° in a current of hydrogen, and is repeated in a vacuum furnace at a vacuum of 10^{-3} mm Hg. The purity of beryllium obtained after two successive meltings was 99.8% (the balance is oxygen).

The high-temperature variant of the above process, which is used at a plant in the USA, employs an electrolyte consisting of 13 to 15% $BeCl_2$ and an equimolar mixture of sodium chloride and potassium chloride. The melting point of the electrolyte is 760 to 790°, but as the $BeCl_2$ concentration decreases during the electrolysis the melting point increases and finally reaches 900 to 925°. At the end of the electrolysis the cell contents are transferred into another vessel; the electrodeposited beryllium accumulates in the bottom layer of the melt. The upper layer, which contains only a small amount of beryllium entrapped in the salts, is removed and returned to the preparation of fresh portions of electrolyte, while the bottom layer, which contains the bulk of the beryllium, is crushed to a particle size of 100 to 150 mm. The metal, remaining after the salts are washed out, contains 99.4 to 99.5% Be.

In the USSR, the electrolytic production of beryllium was improved by employing exchangeable cathodes instead of using a nickel crucible as the cathode; this made it possible to eliminate the need for transferring the whole electrolyte to another vessel. Before the cathodes are changed the electrolyte is heated from 350 to 370—380°, to increase its fluidity to a maximum and to ensure its drainage into the bath during the withdrawal of the cathode. After cooling to room temperature the cathode and the metal are washed to remove the bulk of the electrolyte and the beryllium deposit is separated into two fractions (according to particle size) which are washed with alkali, water and nitric acid (as described above) and the fine fraction (-2 mm), which is more contaminated, is subjected to an additional purification. The beryllium obtained after remelting is of a degree of purity which satisfies the specifications for its use in nuclear reactors as neutron moderator material.

A continuous process for the production of beryllium by electrolysis of the chloride, which was recently proposed, involves passing mercury (which serves as the cathode) through the electrolyte (using a graphite anode); the beryllium deposits on the mercury forming an amalgam (or, more accurately, a suspension of mercury beryllide in mercury) from which the beryllium is recovered by vacuum distillation of the mercury. It should be mentioned that this process has not as yet been tested on a scale larger than that of laboratory experiments.

The electrolytic production of beryllium has the advantage of the removal of impurities during the electrolysis and the disadvantages of a relatively low productivity and low current efficiency.

The approximate concentrations of impurities in beryllium produced by electrolysis of the chloride is as follows (in%):

Fe	0.1—0.02	Cu	0.02—0.07
Mn	0.001	Si	0.01
Ni	0.02—0.05	Cr	0.003

Thermal reduction of beryllium fluoride with magnesium

The selection of the starting halide and reducing agent for the production of beryllium is based on the facts that the melting and boiling points of beryllium fluoride are higher than those of beryllium chloride (which makes it possible to increase the process temperature to the melting point of beryllium without the need for elevated pressures and for the more

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complicated equipment) and that magnesium whose affinity for fluorine is greater than that of beryllium does not form an alloy with beryllium.

The reduction of beryllium fluoride by magnesium involves the reaction

$$BeF_2 + Mg = Be + MgF_2 + \approx 36 \text{ kcal.}$$

A flow sheet for the production of beryllium by thermal reduction with magnesium, including the production of beryllium fluoride from the oxide, is shown in Figure 211.

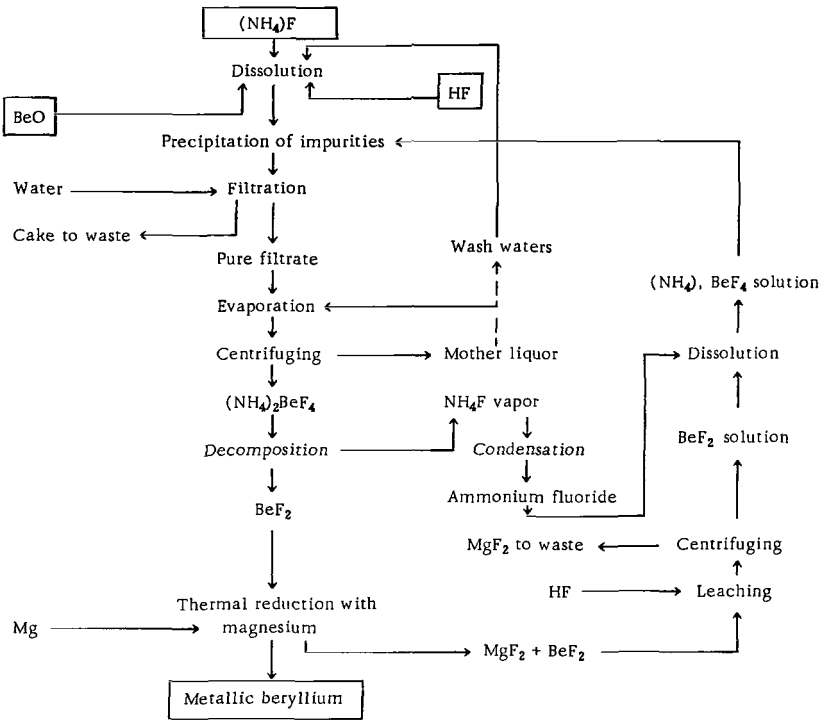

FIGURE 211. Flow sheet for the thermal reduction of beryllium fluoride by magnesium.

Production of the fluoride. High-purity beryllium fluoride is used in the process. It is prepared by thermal decomposition of ammonium fluoberyllate $(NH_4)BeF_4$ which is produced as follows. Technical beryllium oxide or hydroxide, of a low aluminum content, is dissolved in a hot aqueous solution of ammonium bifluoride (NH_4HF_2) or hydrofluoric acid, or a mixture of both. The dissolution is carried out in a steam-heated reactor fitted with a stirrer. The hydrofluoric acid (whose starting concentration in the solution reaches 85 g/l) is neutralized by an excess of beryllium oxide, which settles on the bottom of the reactor. The beryllate solution formed through the reaction

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$$BeO + 2NH_4HF_2 = (NH_4)_2BeF_4 + 2H_2O$$

is transferred by decantation to a second reactor in which it is treated with ammonium sulfide in order to precipitate the heavy metals. The precipitate is separated by filtration; the filtrate (with a Be content of ~ 20 g/l) is evaporated and allowed to crystallize in rubber-lined evaporators. Since the crystallization takes place during the evaporation, the amount of mother liquor returned to the process does not exceed 5% of the total volume of the liquid phase. The crystals are separated from the mother liquor in continuously operating stainless steel centrifuges. The concentration of contaminants in the fluoberyllate crystals is small (~ 0.02% Al and ~ 0.02% Fe). The silicon content is not of importance since the silicon is separated during the subsequent decomposition stage.

The fluoberyllate crystals are decomposed by heating to 950° in graphite crucibles placed in induction or gas furnaces. The decomposition reaction is:

$$(NH_4)_2BeF_4 \rightarrow BeF_2 + NH_4F.*$$

Fresh portions of fluoberyllate are added to the crucible during the course of the decomposition process (which begins at 125°). The ammonium fluoride vapors formed in the decomposition are evacuated through the top of the crucible into a cooled iron condenser. The condensed ammonium fluoride** is returned to the dissolution of the beryllium oxide. During the decomposition the silicon is volatilized as SiF_4. The molten beryllium fluoride is poured into graphite molds in which it solidifies as a vitreous substance containing up to 0.02% Al, 0.02% Fe, and 0.01% Si.

Reduction. Beryllium fluoride is reduced with magnesium at the lowest possible temperature (800 to 1000°) at which the reaction products are still in the solid state (the melting point of BeF_2 is about 800°, of magnesium 650°, and of beryllium and magnesium fluoride 1250 to 1300°). When the reduction is completed, the temperature is raised to 1300° causing the whole reaction to melt. The melting point is reduced and the fluidity of the slag is increased by using excess beryllium fluoride, which forms with the magnesium fluoride a slag whose melting point is near the melting point of beryllium. The presence of an excess of beryllium fluoride also causes a slow-down in the reaction rate (the reaction is strongly exothermic). The introduction of beryllium fluoride causes no contamination of the metal and favors the formation of large beryllium buttons. After melting the charge in a graphite crucible at 1300°, the beryllium buttons are collected in a compact ingot which floats on the surface of the slag. Beryllium solidifies first when the crucible contents are cooled. Thus, solid beryllium may be withdrawn from the molten slag bath. The residual liquid slag is poured into a pan. The slag is crushed and treated with ammonium fluoride or hydrofluoric acid. As a result of this treatment, BeF_2 is dissolved while the magnesium fluoride remains as an insoluble residue. The BeF_2 solution is filtered and taken for the dissolution of the ammonium fluoride.

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* [sic.]

** Actually, the volatile product of the fluoberyllate decomposition — ammonium fluoride — decomposes in accordance with the equation $NH_4F \rightarrow NH_3 + HF$ and at low temperatures the equilibrium shifts to the right-hand side. Thus, further condensation results in the precipitation not of NH_4F but of a $NH_3 \cdot HF$ compound having the approximate formula $NH_3F \cdot 0.5\,HF$ and melting at 83°.

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A diagram of the furnace used for the reduction is shown in Figure 212.

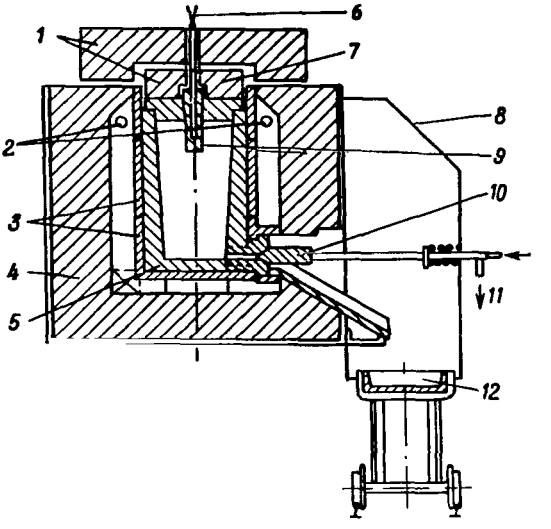

FIGURE 212. Diagram of a furnace for the reduction of beryllium fluoride, fitted with a device for bottom discharge:

1—removable refractory lids; 2—gas burners; 3—lining rings; 4—chamotte brick lining; 5—graphite crucible; 6—thermocouple; 7—crucible lid; 8—exhaust hood; 9—rod; 10—discharge valve; 11—water cooling; 12—pan for the slag.

The beryllium produced by thermal decomposition with magnesium is contaminated by magnesium, beryllium fluoride, magnesium fluoride, and other impurities (~ 0.1% Al, ~ 0.1% Fe, 0.05% Si, 0.05% Cu, 0.05% Mn). To permit its use in the metallic form, beryllium produced by thermal reduction with magnesium must be purified by vacuum melting (which removes a large fraction of the impurities). The approximate concentration of impurities in beryllium produced by thermal reduction with magnesium and purified by vacuum melting is shown below (in%):

Fe	0.08—0.10
Al	0.02—0.03
Si	0.01—0.03
Mn	0.01—0.02

109. VACUUM MELTING OF BERYLLIUM

In modern beryllium production, the main purpose of the melting is the purification of beryllium produced by thermal reduction with magnesium since it is not as yet possible to produce beryllium parts with satisfactory mechanical properties from cast beryllium.

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The main difficulty of the melting is that the beryllium produced has a coarse-grained structure which, because of the anisotropic properties of beryllium crystals, makes the ingot difficult to work by pressure and produces a low-quality surface upon cutting. Studies are now carried out to improve the melting and casting processes in order to eliminate these disadvantages.

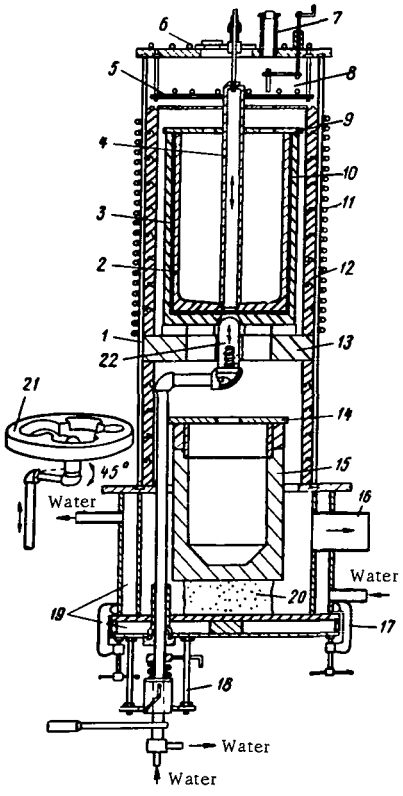

FIGURE 213. Furnace for the melting and casting of beryllium.

1—quartz tube; 2—beryllium oxide crucible; 3—graphite crucible-heater; 4—stopping lever made of beryllium oxide; 5—copper lid; 6—water cooling; 7—viewing tube; 8—shutter; 9—zircon lid; 10—beryllium oxide packing; 11—induction coil; 12—shaped and grooved bricks; 13—graphite ring; 14—pan lid; 15—graphite pan; 16—to vacuum pump; 17—fastening clamp; 18—mechanism for holding and turning the stopping lever; 19—water jacket; 20—bricks; 21—cross piece (the bottom stopper moves between the cross-piece projections during the pouring); 22—bottom stopper made of BeO.

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Because of the high reactivity of molten beryllium, difficulties are encountered in the selection of materials for crucibles, pans, stopping levers, and other parts which come in contact with the molten metal. The most suitable materials are beryllium oxide (although it is expensive and causes some contamination of the metal with oxygen) and graphite, in spite of the fact that graphite and beryllium form a carbide and that graphite absorbs a noticeable amount of molten beryllium. Pans are made of graphite, and a layer of beryllium carbide powder forms at the graphite-beryllium boundary during the casting. In order to prevent interaction between beryllium carbide and moisture (which leads to the formation of gases which may dissolve in the beryllium), the carbide is removed completely by brushing and when not used the pans are stored in a furnace at 200°.

Because of the high affinity of beryllium for oxygen, it is impossible to use any gas (including inert gases, from which the thorough removal of oxygen is very difficult) as a protective atmosphere, and high-quality metal is produced only by melting in vacuum. The melting and casting of beryllium are usually combined (Figure 213).

110. PRODUCTION OF SOLID BERYLLIUM BY POWDER METALLURGY TECHNIQUES

At present, powder metallurgy is the main method for the production of high-quality beryllium products.

The starting beryllium powder is prepared by grinding:

1) beryllium turnings made by cutting of beryllium ingots cast in a vacuum;

2) beryllium flakes or sponge, made by electrolysis of beryllium chloride;

3) metal prepared by distillation.

The most widely used method is the first one. The turnings are ground in a water-cooled attrition mill (with beryllium-faced discs) operating in a dry inert gas atmosphere. The finely ground powder is sieved in a vibratory sieve, the fraction -0.074 mm is collected and the fraction larger than 0.074 mm returned to grinding.

Solid products may be made from beryllium powder by hot pressing, cold pressing and subsequent sintering, forging, extrusion, and rolling. The following are the main methods used for manufacturing various beryllium products:

1. production of large rods for subsequent turning on a lathe:

a) hot pressing in vacuum,

b) hot pressing of powder which has been preliminarily pressed in air, taking measures to prevent oxidation;

2. production of parts of a required shape:

a) warm pressing,

b) high-temperature pressing in air, with protective measures against oxidation,

c) hot stamping of bars,

d) high-temperature forging of rods made of the powder;

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3. production of semiproducts which are worked to the final dimension by pressure working (extrusion, forging, rolling):

a) any method mentioned in paragraphs 1 and 2;

b) hydrostatic or pneumatic hot pressing in a vacuum.

Hot pressing in vacuo is carried out under a pressure of 10 to 20 kg/cm^2 at 1050° using powder with a particle size below 0.074 mm. The pressing is carried out in steel dies and pressure is produced by the punch weight.

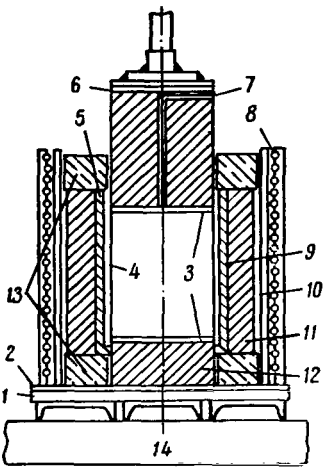

FIGURE 214. Die used for the hot pressing of beryllium blocks 152.4 and 304.8 mm in diameter.

1—boiler-iron plate; 2—intermediate plate; 3—steel lining of the punch; 4—steel insert; 5—thermocouple insertion point, for measuring the die-body temperature; 6—intermediate plate; 7—device for measuring the temperature of the upper punch; 8—induction coils; 9—graphite tube; 10—quartz tube; 11—die body; 12—lower punch; 13—special refractory rings; 14—press base.

Hot pressing in air resembles in principle the pressing in vacuum but is carried out in graphite dies which burn and thus prevent oxidation of the powder; an advance pressing of the beryllium powder also prevents oxidation. Since appreciable interaction between the powder and the die walls may take place at 1100 to 1200°, leading to the formation of beryllium carbide, the reaction between the graphite and the beryllium walls is prevented by coating the graphite walls of the die with a protective layer (beryllium oxide coating or low-carbon steel lining).

The cross section of a die used in the production of large parts is shown in Figure 214. The graphite body has two linings: an external graphite lining which facilitates dismantling, and an inner steel lining with a longitudinal cut which facilitates the removal of the punch. The inner and outer surfaces of the steel lining are chromium plated to protect the steel against interaction with the graphite and the beryllium. The punches and base blocks are made of low-carbon steel. The die is placed within a quartz tube which prevents arcing between the graphite and the induction coil and serves as thermal insulation.

During the hot pressing, the temperature is measured with the aid of a thermocouple. The wall thicknesses of dies used for the pressing of blocks 152.4 and 304.8 mm in diameter were 50.8 and 76.2 mm, respectively. The blocks made in these dies weighed 1.8 to 13.6 kg. The die was heated by means of a high-frequency generator; the power required to heat blocks 152.4 and 304.8 mm in diameter was about 30 and about 50 kwh respectively. An 80-ton press was used for pressing.

The pressing involves the following operations. The die is mounted on the press and beryllium powder is fed into the die cavity. The die is then heated slowly (over 1.5 to 2 hours) to 1100°; a pressure of 50 kg/cm^2 is applied at 1000° and is increased to 70 kg/cm^2 as the temperature reaches 1100°. This pressure is maintained for 30 to 40 minutes at 1100°.

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The density of hot-pressed blocks made at 1100° under a pressure of 50 to 70 kg/cm^2 is close to the theoretical.

Warm pressing is carried out in a vacuum at 550 to 600°, under a pressure of 4 to 14 tons/cm^2. This method makes it possible to produce a metal of theoretical density, with a fine-grained structure, great hardness and strength. The bars made by warm pressing are cold-hardened to a noticeable extent, and their properties resemble those those of cold-worked metal. The warm pressing is carried out in dies made of high-speed steels (18% W, 40% Cr, 1% V) or refractory steels.

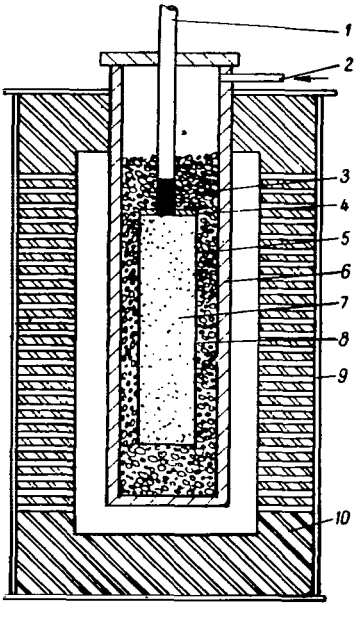

FIGURE 215. Diagram of installation for the hot hydrostatic pressing of beryllium powder.

1—vacuum line; 2—high-pressure line; 3—graphite filter; 4—steel plate; 5—steel envelope; 6—pressure chamber; 7—beryllium powder; 8—silicon carbide packing; 9—gas burner heads; 10—refractory bricks.

Beryllium powder is also pressed at 800° (i.e., at a temperature intermediate between warm and hot pressing) and pressures up to 3 tons/cm^2.

Hot stamping involves the compaction (at 400 to 600°) of semi-finished bars made by cold pressing, with subsequent sintering and hot or warm pressing to parts of the required shape.

Forging is used to convert beryllium powder into parts by pressing in shaped steel dies. The die with the powder is heated in an inert atmosphere to 1000 to 1150°, and is then transferred to the die support (which is preheated to 400 to 800°) and pressed under 150 to 700 kg/cm^2. This method may be used to produce parts weighing up to 7 kg, and having a shape and dimensions close to the required.

Hot hydrostatic pressing is a promising method for the production of parts of a complicated shape. The nature of this process was described in the chapter on molybdenum.

In one variant, the hot hydrostatic pressing of beryllium powder is carried out at 1000 to 1100°, under a pressure of 7 to 20 atm, using argon or some other inert gas as a protective atmosphere. The beryllium powder is fed into a steel die whose inner surface has the same shape as the part to be produced. The die is then placed in a tube in the heating zone (Figure 215). The space between the tube and the outer surface of the steel die is packed with a nonsinterable material impermeable to gases (e.g., silicon carbide). Argon is then pumped into this space until the above-mentioned pressure is reached, while the inner space of the die containing the beryllium powder is evacuated (by connecting to a vacuum system) to a residual pressure of 0.05 mm Hg.

In addition to the above method use is made of "warm" hydrostatic pressing in molten lead at lower temperatures but higher pressures.

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The various powder metallurgy methods produce beryllium powders of markedly differing mechanical properties. Beryllium with the best properties is prepared by hot pressing in vacuum.

111. PURIFICATION OF TECHNICAL GRADE BERYLLIUM

As mentioned above, the primary purification of beryllium produced by thermal reduction with magnesium is accomplished by vacuum melting of the metal.

Thorough purification of beryllium is accomplished through vacuum distillation, soluble-anode electrolysis, and zone melting in electron-beam furnaces.

Vacuum distillation is carried out at $\sim 1400°$ at a residual pressure of $\sim 10^{-4}$ mm Hg.

The condensation of beryllium vapors in a cold condenser results in the removal of a noticeable fraction of impurities such as iron, carbon, and boron. However, the aluminum, silicon, and manganese contents remain practically unchanged since the difference between the vapor pressure of these impurities and beryllium is small.

A high-efficiency variant of the vacuum distillation of beryllium has been developed in the USSR; it is based on condensation on heated surfaces. This method makes it possible to reduce the manganese, aluminum, and silicon concentration in the distilled beryllium to 0.001 to 0.002%, and to increase the purity of the metal to 99.98% Be /26/. The electrolytic purification is based on the fact that most of the impurities present in the technical grade metal (Al, Fe, Ni, etc.) are more electropositive than beryllium. Thus, during anodic dissolution they are not dissolved in the electrolyte and do not reach the cathode. The concentrations of the main impurities in electrolytically refined beryllium is: Fe 0.005 to 0.006%, Cu 0.003%, Mn $n \cdot 10^{-4}$%, Zn and Si $n \cdot 10^{-3}$%, and B less than 0.3 g/ton.

The impurity contents of beryllium prepared by distillation or by electrolytic refining are similar, and the metal satisfies the specification for nuclear uses.

Zone melting of beryllium in electron-beam furnaces is a promising method presently under development.

112. PRODUCTION OF BERYLLIUM ALLOYS

As a rule, beryllium alloys are not prepared by direct alloying of the components (e.g., copper with beryllium, nickel with beryllium, aluminum with beryllium, etc.) but by thermal reduction with metals or reduction with carbon in the presence of the second alloy component. This produces beryllium master alloys (alloys which are used to introduce the alloying components into the alloy composition).

Beryllium alloys are occasionally made by powder metallurgy techniques, i.e., by mixing the powdered beryllium and second component, pressing the mixture and sintering. For instance, such techniques have been recently used for the production of a nickel-beryllium master alloy containing 10 to 20% Be, and beryllium alloys with rhenium, tungsten, and other refractory metals.

Master alloys of beryllium with aluminum and copper have been prepared by thermal reduction of beryllium chloride or fluoride with magnesium-aluminum or magnesium-copper alloys.

For this use, beryllium is taken in the form of sodium fluoberyllate:

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$$Na_2BeF_4 + \underset{\text{alloy}}{Mg\text{-}Al} \rightarrow \underset{\text{master alloy}}{Be\text{-}Al} + MgF_2 + 2NaF.$$

Beryllium chloride is reduced in a molten salt medium (molten sodium and potassium chlorides). The reduction of beryllium chloride by a copper-magnesium alloy (20% Mg) at 950° in the presence of a 200% excess of beryllium chloride (above the stoichiometric amount) produces a copper-beryllium alloy containing 1.7 to 1.8% Be and 13 to 14% Mg.

The reduction involves the reaction:

$$BeCl_2 + \underset{\text{alloy}}{Mg\text{-}Cu} \rightarrow \underset{\text{master alloy}}{Be\text{-}Cu} + MgCl_2.$$

In order to remove the magnesium the alloys are remelted in vacuo; as a result, the beryllium concentration is increased to ~ 2%.

Master alloys containing up to 3% Be are produced in the reduction of $BeCl_2$ by aluminum alloys.

Copper-beryllium and nickel-beryllium master alloys are also produced by thermal reduction (in an electric furnace) of beryllium oxide by carbon in the presence of the metal forming the alloy with beryllium. The direct reduction of beryllium oxide with carbon yields beryllium carbide Be_2C rather than beryllium. In the presence of a metal with a high boiling point (e. g., copper) the reduction of beryllium oxide takes place as follows:

$$BeO(solid) + C(solid) + xCu(liquid) \rightarrow BeCu_x(liquid) + CO(gas); \quad (1)$$

$$2BeO(solid) + 3C(solid) + xCu(liquid) \rightarrow Be_2C,\ xCu(liquid) + 2CO(gas); \quad (2)$$

$$2BeCu_x(liquid) + C(solid) \rightarrow Be_2C,\ xCu(liquid); \quad (3)$$

$$BeO(solid) + Be_2C,\ xCu(liquid) \rightarrow 3BeCu_x(liquid) + CO(gas). \quad (4)$$

Reaction (1) takes place at low beryllium concentrations in the alloy, reactions (2) and (3), as well as reaction (1), take place as the beryllium concentration is increased, and reaction (4) takes place only in the presence of large amounts of beryllium carbide.

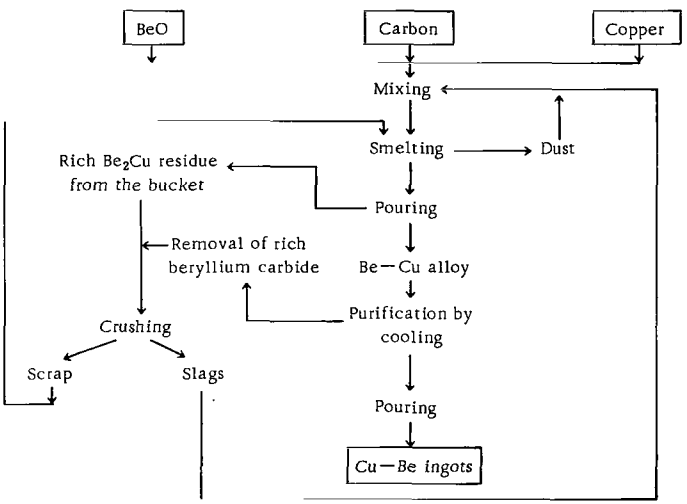

FIGURE 216. Flow sheet for the smelting of copper-beryllium alloys by thermal reduction in an electrical furnace.

The optimum process temperature (at which the formation of beryllium carbide is still slow while the losses through vaporization of copper and beryllium are small) ranges from 1800 to 2100°; the best results are obtained at 1950°.

During the smelting beryllium oxide and the graphite form a fine suspension in the molten alloy while the carbide Be_2C dissolves in considerable amounts in the melt at the reduction temperature. However, the solubility of Be_2C in the alloy decreases as the temperature is reduced to 900 to 1000° and almost

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complete removal of the carbide may be achieved by cooling and mixing the alloy before it is discharged from the furnace. The BeO and C flow on the surface together with the carbide.

A flow sheet for the smelting of copper-beryllium alloys in an electrical arc furnace is shown in Figure 216, and a diagram of the furnace is shown in Figure 217. The charge is composed of beryllium oxide, copper, recycled slags, and coal of low ash content. For example, 100 kg of BeO is mixed with 835 kg of copper, 185 kg of slag, 150 kg of scrap, and 67 kg of coal. When compounding the charge, the amount of BeO taken is calculated to bring the Be content of the alloy to ~ 5% and the coal is taken in a 10% excess above the stoichiometric amount needed for the reduction of the BeO.

After the mixing the charge is fed to a three-phase electrical furnace with three short electrodes fastened with the aid of adapters to water-cooled copper sockets. The sockets are fastened on hollow steel electrode holders which are connected to the copper bus bars supplying the current. At the end of the smelting, the current is turned off, the electrodes are withdrawn, and the melt is discharged (by tilting the furnace) through the tap hole into a carbon-lined steel bucket; the temperature of the melt during the pouring is 1300 to 1500°.

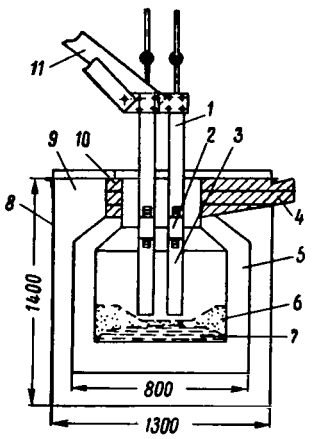

FIGURE 217. Diagram of a three-phase furnace for the smelting of copper-beryllium alloys.

1—water-cooled steel electrode; 2—water-cooled copper socket; 3—graphite electrode; 4—BeO tap hole; 5—carbon lining; 6—charge; 7—Cu—Be alloy; 8—steel jacket; 9—refractory lining; 10—BeO bricks; 11—[electrical] leads.

The beryllium carbide, beryllium oxide and carbon float on the surface and remain in the bucket during the pouring. The melt is cast into a ceramic crucible in which it is cooled to 900 to 950° with continuous stirring. When the temperature drops to 900 to 950°, the impurities are removed from the surface and the melt is cast in graphite molds. The slag is ground in a ball mill, which is lined with copper-beryllium alloy plates.

The coarse fraction from the grinding (scraps) contains 6.5%Be, 90% Cu, 2% C, and 1.5% O, while the fine fraction (slag) contains 8% Be, 65% Cu, and 20% O. The scraps and slags are returned to the smelting.

The productivity of the furnace is 2.6 tons of copper-beryllium alloy per day, the consumption of electrical energy is 2.75 kwh/kg. The alloy obtained by thermal reduction in an electric furnace contains 4 to 4.5% Be, 0.1% Fe, 0.08% Si, and 0.06% Al.

Nickel-beryllium and some other master alloys are prepared by similar methods.

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113. TOXIC PROPERTIES AND SAFETY MEASURES

Beryllium and its compounds are very toxic, and when absorbed in the body they cause profound irreversible changes.

Beryllium compounds attack the respiratory organs, causing acute and chronic irritation of the nasopharynx, the bronchial tubes, and the lungs; they affect the skin and mucous membrane of the eyes, causing acute and chronic dermatitis, ulcers, eczemas, and conjunctivitis; the gastrointestinal tract is gravely affected when beryllium enters the body with the foodstuffs.

Acute chemical pneumonitis (resembling phosgene poisoning) and berylliosis (a chronic beryllium poisoning accompanied by general weakness, breathlessness, serious loss of weight, and increased temperature) are particularly dangerous diseases caused by beryllium poisoning. Acute pneumonitis is caused by soluble beryllium compound concentrations (in air) above 100 $\mu g/m^3$, and berylliosis is caused by concentrations above 0.01 $\mu g/m^3$, by the gradual accumulation of beryllium in the body. Berylliosis is often fatal.

Metallic beryllium and its oxide, sulfate, fluoride, hydroxide, and chloride (i.e., all the compounds which are used in beryllium manufacturing) are especially toxic. Beryllium ores and concentrates are somewhat less toxic. Obviously, the danger of beryllium poisoning is greater in industrial processes involving crushing, sieving, filtration, and evaporation, i.e., processes in which beryllium or its compounds are in a finely dispersed or a dissolved state which facilitates their absorption by the human body.

Because of these properties of beryllium and beryllium compounds, personnel protection and safety measures in beryllium manufacturing are highly important. In general, the main safeguards are as follows.

1. All equipment, pipelines and other transport devices should be hermetically sealed to the greatest possible extent; this should be designed for each type of equipment. Full sealing is required for equipment such as vacuum filters, centrifuges, driers, electrical furnaces, hot-pressing presses, etc.

2. The design of beryllium plants should be based on the three-zone principle:

1) technological equipment and transportation zone;

2) a zone for decontamination and repair of the equipment;

3) personnel residence zone, for personnel supervising the technological processes by remote control; this zone must be completely isolated from the first and second zones by thick walls.

A sufficiently large distance between the beryllium plant and residential or communal buildings of towns or villages in the vicinity of the plant is also of great importance for preventing berylliosis in human beings and animals.

3. The technological process as a whole and the individual operations must be automated and mechanized to the greatest possible extent, and remote control should be used.

4. Provision must be made for a powerful ventilation system, including the exhausting devices installed in individual units, using only hermetically sealed exhaust pumps, exhaust hoods, and edge exhausters.

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5. Filtration of gases and vapors discharged during the technological process, collection of beryllium-containing substances, and provision of special storage rooms for the solid wastes. Stores should also be constructed in accordance with these safety principles.

6. Use of personal safety equipment (goggles, respirators, gas masks, pneumatic helmets, pneumatic suits) and working suits of special cloths ("lavsan", coarse wool cloths, and polyvinyl chloride tissues) which are removed in a special chamber before the personnel leaves the plant.

7. A preliminary (for new personnel) and subsequent regular periodic medical inspections.

8. Regular control of the beryllium content in working rooms and in the vicinity of the plant.

The personnel health hazards in beryllium plants may be completely eliminated by proper manufacturing procedures and by the observance of all safety precautions (of both personal and general nature) in the processing of beryllium and its compounds.

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Chapter XIII

LITHIUM

114. GENERAL DATA ON LITHIUM

Lithium was discovered in 1817 by Arfvedson, a Swedish chemist, in the mineral petalite. Its name (from the Greek word "litheos" — stone) comes from the fact that it was discovered in a mineral, in contrast to potassium which at that time was obtained from the ash of plants. In 1818 Davy prepared for the first time lithium metal by decomposition of lithium oxide with electric current. Comparatively large amounts of lithium were prepared only in 1854 by electrolysis of fused lithium chloride. In Russia, the study of lithium and lithium compounds was started by Solov'ev in 1824.

Properties of lithium

Lithium belongs to Group I of the periodic table. Its atomic weight is 6.940, its atomic number is 3. It has two isotopes with mass numbers 6 and 7 (their concentration in natural lithium is 7.52 and 92.48% respectively).

Lithium is a silvery-white metal, and is the lightest of all known metals. Lithium vapors color a flame red. The arc spectrum of lithium lies in the visible, infrared and ultraviolet.

The physical properties of lithium are tabulated below.

Density, g/cm^3:	
of natural Li	0.531
of Li^6	0.460
of Li^7	0.537
Lattice type and parameters	Body-centered cubic, a = 3.5023 Å
Thermal neutron capture cross section, barns:	
of Li^6	910
of Li^7	0.033
of natural Li	67 ± 2
Melting point, °C	180.5
Boiling point, °C	1327
Heat of fusion, cal/g	100
Heat of vaporization, cal/g	4636
Vapor pressure (mm Hg) at various temperatures (°C):	
180.5	$1.41 \cdot 10^{-10}$
502	$3.68 \cdot 10^{-3}$
727	0.782

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1002	41.0
1177	91.0
Heat capacity, cal/g, °C (at 0—100° C)	0.90
Thermal conductivity (at 0—100° C), cal/sec · cm, °C	0.17
Linear expansion coefficient (20 to 180° C)	$5.6 \cdot 10^{-5}$
Electrical resistance (ohm · cm · 10^{-6}) at various temperatures:	
0° C	8.55
99.3° C	12.7
230° C	45
Normal electrode potential (18° C), V	-3.02
Electron work function, eV	2.34—2.46
Tensile strength, kg/mm^2	11.8
Modulus of elasticity, kg/mm^2	500
Elongation, %	50—70

The ionization potential of a lithium atom (i. e., the energy required to remove an electron) is 5.37 eV, i. e., higher than the ionization potentials of the other alkali metals (Na 5.09, K 4.32, Rb 4.19, Cs 3.86 eV). As a result, the chemical activity of lithium is lower than that of the other alkali metals, and lithium has a polarizing effect on the atoms of other elements. It has a great tendency towards the formation of stable complex compounds, and yields no peroxides when oxygen acts directly on metallic lithium.

As compared with the other alkali metals, lithium has the highest potential of electrolytic deposition from aqueous solutions, a fact which is related to the large hydration energy of lithium ions. As a result of the strong hydration of lithium ions the hydrated ions are characterized by their large radius and low mobility, in spite of the fact that lithium ions are smaller than the ions of the other alkali metals. On the other hand, the deposition potential of lithium from molten salts is the smallest among the alkali metals, which is in agreement with the values of the ionization potentials.

Lithium is a very ductile metal, with a very great elongation, and is easily worked by rolling, drawing, forging, stamping, and extrusion. The electrical resistivity of lithium is about 1/5 that of silver and 11 times that of mercury.

The natural isotopes of lithium are nonradioactive; radioactive isotopes may be produced by various nuclear reactions. The most important nuclear reaction involves the natural isotope Li^6 — capture of a neutron followed by decay into an α-particle and a tritium atom*:

$$Li_3^6 + n_0^1 = He_2^4 + H_1^3.$$

The capture of a neutron by the natural Li^7 isotope leads to the creation of an α-particle and the liberation of a large amount of energy:

$$Li_3^7 + n_0^1 \rightarrow Be_4^8 \rightarrow 2He_2^4.$$

The chemical activity of lithium is smaller than that of the other alkali metals. However, even at room temperature lithium slowly reacts with the oxygen and nitrogen from dry air yielding the oxide Li_2O and nitride Li_3N. The $Li_3N : Li_2O$ ratio in the product is 3 : 1. Lithium nitride is decomposed by water, yielding ammonia.

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* Tritium is a hydrogen isotope with atomic number 3.

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Lithium burns in oxygen above 200°, yielding the oxide. Lithium causes vigorous decomposition of water, with the evolution of hydrogen and the formation of lithium hydroxide, as follows:

$$2Li + 2H_2O = 2LiOH + H_2.$$

Lithium hydride LiH (with a melting point of 680°) is formed when lithium is heated in nitrogen to 350 to 400°.

Heating a mixture of lithium and carbon leads to the formation of lithium carbide Li_2C_2, which decomposes water, with the evolution of acetylene.

Lithium and gaseous ammonia form the amide:

$$2Li + 2NH_3 = 2LiNH_2 + H_2.$$

At elevated temperatures lithium reacts with chlorine and with bromine, iodine, and sulfur vapors yielding the respective halides and the sulfide; lithium ignites as a result of its reaction with nitric acid, and forms an amalgam with mercury. The reaction of lithium with carbon dioxide leads to the formation of lithium oxide or carbonate. This eliminates the possibility of using carbon dioxide fire extinguishers for extinguishing burning lithium.

Most metals and alloys are attacked by molten lithium.

Among the steels, chromium steels are the most resistant to lithium. Of all steels tested, the best results were obtained with steel 1Kh12MV4B (the corrosion rate at 800° was 0.7 mm/year). Pure nickel and the alloy Inconel (11 to 15% Cr, 70% Ni, 10% Fe) have a satisfactory resistance to molten lithium up to 225° but are attacked rapidly above 600°.

Niobium, tantalum, and molybdenum are most resistant to the effect of lithium at up to 1000° (their solubility in lithium at 1000° is 10^{-4}%). Zirconium and titanium have a limited resistance to lithium at 1000°.

Quartz, glass, and porcelain are rapidly dissolved by lithium at temperatures above 200°.

The properties of lithium compounds

Oxides. Lithium and oxygen form the oxide Li_2O and the peroxide Li_2O_2.

Lithium oxide is a colorless crystalline substance formed when lithium is oxidized in a current of oxygen above 200° or when lithium hydroxide, carbonate, or nitrate are decomposed at 750 to 880°. The heat of formation of Li_2O is 143.2 kcal/mole. Lithium oxide has a face-centered cubic lattice (CaF_2 type) with a lattice parameter of 4.62 Å; it has a high thermal stability, a high melting point (above 1400°), and starts to volatilize at 1000 to 1040° (a sharp increase in the volatility of lithium oxide is observed in the presence of water vapor, due to partial conversion of the oxide to the more volatile lithium hydroxide). Li_2O dissolves slowly (as compared with the other alkali oxides) in water, with the evolution of large amounts of heat and the formation of lithium hydroxide. Li_2O absorbs CO_2 from the air, with the formation of lithium carbonate. Metals (even noble metals) are attacked rapidly by lithium

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oxides. At temperatures above 1000° aluminum, magnesium, and silicon reduce the oxide to lithium metal.

Lithium peroxide Li_2O_2 cannot be produced by direct combination of lithium metal and oxygen, but can be produced indirectly. For instance, it is formed in the interaction of an alcoholic solution of lithium hydroxide with hydrogen peroxide. The peroxyhydrate — $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ — a white, crystalline, sparingly-soluble substance is formed in the presence of an excess of the alcohol; the peroxyhydrate is converted to lithium peroxide by drying over phosphorus pentoxide. The heat of formation of lithium peroxide is 151.8 kcal/mole. Li_2O_2 is thermally unstable, and completely decomposes (to lithium oxide and oxygen) upon heating to 195°.

Lithium hydroxide is a white substance with a density of 1.46. It can be prepared by dissolving Li_2O in water, or through a substitution reaction between lithium sulfate and potassium hydroxide (or barium or calcium hydroxides), and through a substitution reaction involving the decomposition of lithium carbonate by calcium hydroxide:

$$Li_2CO_3 + Ca(OH)_2 = 2LiOH + CaCO_3.$$

The evaporation of a LiOH solution in a CO_2-free gas atmosphere causes the precipitation of the crystalline hydrate $LiOH \cdot H_2O$ which upon heating to 600° is readily converted first to LiOH and subsequently (at 780°) to Li_2O. The solubility of lithium hydroxide in water is much lower than that of the other alkali hydroxides. The solubility of the hydroxide LiOH and the crystalline hydrate $LiOH \cdot H_2O$ increases with increasing temperature; thus the solubility of LiOH in water at 0 and 100° is 12.7 and 17.5 g/100 g water, while the solubility of $LiOH \cdot H_2O$ at 10 and 80° is 22.3 and 26.8 g/100 g water respectively. The melting point of LiOH is 450°. At about 1000° lithium hydroxide is completely decomposed yielding lithium oxide and water; the vapor pressure of water over lithium hydroxide at various temperatures is listed below:

Temperature, °C	520	610	670	724	812	924
Vapor pressure, of H_2O, mm Hg	2	23	61	121	322	760

Lithium hydroxide is very corrosive; it attacks glass and porcelain even at room temperature and glass or porcelain containers to be used for the storage of lithium hydroxide must be coated with paraffin. The hot hydroxide attacks many metals, oxides and silicates.

Lithium carbonate Li_2CO_3 is characterized by its low solubility (as compared with the solubility of the other alkali carbonates), a fact that is used in the manufacturing of lithium salts. The solubility of lithium carbonate decreases with increasing temperature:

Temperature, °C	0	10	20	50	75	100
Solubility, g/100 g water	1.54	1.41	1.33	1.18	0.87	0.73

The solubility of lithium carbonate in water increases in the presence of sodium, potassium, and ammonium ions (because of the formation of complex compounds) and in the presence of carbon dioxide (because of the formation of the acid salt).

Lithium carbonate melts at 732° and undergoes thermal decomposition at higher temperatures; the decomposition is completed at 1270°. In vacuo (1 mm Hg) the decomposition of Li_2CO_3 starts at 600° and is complete at 800°.

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Lithium bicarbonate $LiHCO_3$ (whose solubility is much higher than that of lithium carbonate) is formed when carbon dioxide is passed through an aqueous suspension of lithium carbonate. When an aqueous solution of the carbonate is boiled it is hydrolyzed to the bicarbonate and LiOH.

Lithium hydride is formed in the reaction between hydrogen and lithium metal:

$$Li + {}^1/_2 H_2 = LiH + 21.6 \text{ kcal}$$

the reaction starts at 380 to 400° and is rapidly completed at 700 to 720°. At higher temperatures the hydride dissociates into the elements.

Lithium hydride is a white solid (the contaminated hydride is gray) with a density of 0.76 to 0.8 g/cm^3; it has a face-centered cubic crystal lattice of the NaCl type (a = 4.1 Å), its melting point is about 680°, and in the molten state it is a good conductor of electricity.

The decomposition of the hydride begins at 500° (the dissociation pressure is 0.07 mm Hg) and is completed at 850°. In a vacuum, volatilization (with partial decomposition) of LiH starts at 220°. LiH is stable in dry air and oxygen at room temperature, it is slowly decomposed by the moisture in humid air, and reacts vigorously with water, with the evolution of hydrogen:

$$LiH + H_2O = LiOH + H_2 + 31 \text{ kcal}.$$

A reaction between lithium hydride and oxygen occurs only at 600 to 700°. Upon heating, lithium hydride reacts with nitrogen yielding the nitride:

$$3LiH + N_2 \rightarrow Li_3N + NH_3.$$

The interaction of lithium hydride with aluminum chloride (in an ethereal solution) yields lithium alumohydride $LiAlH_4$ — a colorless crystalline substance which decomposes at 150° yielding lithium hydride, hydrogen, and aluminum:

$$2LiAlH_4 \rightarrow 2LiH + 3H_2 + 2Al.$$

The alumohydride is extensively used in organic synthesis as a reducing and hydrogenating agent. Lithium borohydride $LiBH_4$, which is an abundant source of hydrogen (hydrogen accounts for nearly 1/5 of its weight), has properties resembling those of the alumohydride. While the reaction of LiH with water liberates 280 liters of hydrogen per kg of hydride, the hydrolysis of lithium borohydride yields 4100 liters of hydrogen per kg. Lithium borodeuteride and borotritide are excellent sources of deuterium and tritium respectively. Thus, nearly 40% of the borotritide consists of tritium.

Lithium nitrate $LiNO_3$ is formed by dissolving lithium carbonate in nitric acid and subsequent evaporation. It is a colorless crystalline substance with a density of 2.4 and a melting point of 252°. Lithium nitrate is hygroscopic and readily dissolves in water with the evolution of a small amount of heat. Lithium nitrate has several known crystalline hydrates: $LiNO_3 \cdot 3H_2O$ (stable between -18 and +30°), $2LiNO_3 \cdot H_2O$ (30 to 65°) and the anhydrous $LiNO_3$ (above 65°). When heated to 600° the nitrate decomposes yielding lithium oxide:

$$2LiNO_3 \rightarrow Li_2O + NO + NO_2 + O_2.$$

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Lithium sulfate is formed when a solution of lithium carbonate is treated with sulfuric acid. Slow evaporation of a solution of Li_2SO_4 in sulfuric acid causes the crystallization of the monohydrate $Li_2SO_4 \cdot H_2O$ while prolonged removal of water by evaporation leads to the formation of anhydrous Li_2SO_4. The solubility of lithium sulfate in water is lower than the solubilities of lithium nitrate and chloride, and it decreases with increasing temperature; thus, its solubility at 0 and 100° is 35.34 and 29.9 g/100 g water respectively.

Li_2SO_4 and the sulfates of the other alkali metals form double salts of the $MeLiSO_4$ and $Me_3Li(SO_4)_2$ types (where *Me* is K^+ or Na^+). Lithium sulfate is sparingly soluble in organic solvents and does not form alums (this fact is used in analytical chemistry and in manufacturing technology for the separation of lithium sulfate from the sulfates of the other alkali metals). Li_2SO_4 is a colorless crystalline substance with a density of 2.22 and a melting point of 860°; at 576° it is subject to a phase transformation (from the monoclinic to the cubic modification).

Halides. Lithium chloride LiCl is produced by dissolving lithium carbonate in hydrochloric acid or by an exchange reaction between lithium sulfate and barium chloride:

$$Li_2SO_4 + BaCl_2 = 2LiCl + BaSO_4.$$

LiCl may also be produced by direct chlorination of lithium metal in the presence of extremely small amounts of moisture. LiCl is a white crystalline substance; it has a salty taste, and it is hygroscopic and readily soluble in water (its solubility increases with increasing temperature). The solubility of LiCl in water at 0 and 22° is 16 and 20 moles/l respectively. Anhydrous lithium chloride crystallizes from aqueous solutions at temperatures above 94°. The monohydrate $LiCl \cdot H_2O$ separates between 94 and 19° while the dihydrate $LiCl \cdot 2H_2O$ crystallizes between +19 and -20.5°.

Anhydrous LiCl has a density of 2.068, a heat of formation (from the elements) of 97.04 kcal/mole, a melting point of 614° and a boiling point of 1337°. At atmospheric pressure volatilization of the chloride starts at 960° and becomes very rapid above 1080°.

In contrast to the chlorides of other alkali metals, LiCl cannot be precipitated from an aqueous solution by an excess of hydrochloric acid since the strong hydration of lithium ions prevents their combination with chloride ions.

In an aqueous solution, lithium and ammonia form a complex — $[Li(NH_3)_n]Cl$.

In contrast to KCl and NaCl, LiCl dissolves in organic solvents — saturated alcohols, ketones, chloroform, pyridine, and higher aliphatic alcohols, yielding organolithium compounds.

Lithium fluoride is prepared by the addition of sodium or ammonium fluoride to solutions of lithium salts. LiF is a white crystalline substance with a melting point of 848 and a boiling point of 1676°. Rapid evaporation of the salt starts at 1100 to 1200° and becomes very rapid above 1270°. The low solubility of LiF in water must be noted; a saturated solution of LiF at 18° contains only 0.26% of the salt. This fact is used in analytical chemistry and in production technology for the separation of LiF from the fluorides of the other alkali metals. Lithium fluoride dissolves in hydrofluoric acid yielding an acid salt — $LiHF_2$. Lithium fluoride is insoluble in organic solvents (acetone, alcohol, pyridine).

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Uses of lithium

The use of lithium and lithium compounds has expanded vigorously during the last decades. Its most important uses are described below.

Nuclear technology and nuclear energy. After the Second World War nuclear energy became one of the most important branches in which lithium is used. Here, the most important use of lithium involves the production of tritium (for thermonuclear reactions) by neutron bombardment of the Li^6 isotope.

The reaction $Li_3^6 + n_0^1 = He_2^4 + H_1^3$ (or $Li^6\ (n, \alpha)T^3$ where T^3 is tritium, the heavy hydrogen isotope, and α is a helium nucleus) is accompanied by the liberation of a huge amount of energy — 4.80 MeV. Thermonuclear technology is based on the interaction of deuterium or tritium nuclei with the formation of helium isotopes (such interaction takes place at temperatures of $10^8 - 10^9$ °K) and the liberation of even larger amounts of energy.

Since tritium is virtually nonexistent in nature, it is produced by irradiation of natural lithium with thermal neutrons, in a uranium reactor (in accordance with the above reaction). The tritium formed may be stored since its half-life is 12.3 years.

A hydrogen bomb, which makes use of lithium deuteride LiD as the solid fuel, is based on both reactions — the nuclear transmutation of lithium with the evolution of tritium, and the transmutation of deuterium reacting with tritium, which are accompanied by the liberation of an extremely large amount of heat, i.e., 22.4 *M*eV per lithium deuteride molecule. Another important application of lithium in nuclear technology involves the use of hydride Li^6H as a fast-neutron shield (both light components of lithium hydride have a strong attenuation effect on fast neutrons).

The large thermal neutron capture cross section and the low density of lithium are the reasons for its use in the so-called "light shielding" — shields for aircraft with nuclear power plants. Lithium metals and lithium compounds (oxide, hydride, etc.) are used as components of nuclear reactor shields (neutron shielding, and shields against the secondary γ-radiation resulting from neutron capture in the shielding material).

It has been suggested that liquid Li^7 be used as a coolant in nuclear reactors. The thermal neutron capture cross section of lithium is only 1/16 that of sodium. However, lithium has the disadvantage of being very corrosive with respect to heat-exchanger materials.

Rockets and jet engines. Many compounds of lithium with boron and hydrogen (hydride, borohydride), as well as lithium metal, lithium perchlorate, and lithium nitrate, are characterized by their high combustion rates and temperature, high flame-propagation velocities, and the evolution of large amounts of heat per unit weight; these facts serve as the basis for the use of the above substances as fuels for rockets, supersonic aircraft, guided missiles, and submarines.

Lubricants. The lithium salts of stearic and other organic fatty acids are the main components of special high-viscosity lubricating greases which are insoluble in water and stable at low temperatures. They do not freeze down to -60° and do not decompose at elevated temperatures (120 to 150° and in some cases up to 200°). Such greases are extensively used in

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aviation, military technique, as lubricants in equipment for arctic uses, as impregnation lubricants for porous bearings (prepared by powder metallurgy) intended for low or high temperature uses, etc.

Ceramics and glass industry. The addition of lithium compounds (carbonate, oxide, titanate, and zirconate) or concentrates (lepidolite, petalite) to the ceramic mixtures used in the production of faience, porcelain, heat-resistant ceramics, and refractories makes it possible to reduce markedly the firing temperature, and to produce denser and mechanically stronger ceramic products with a lower thermal expansion coefficient (i. e., with increased resistance to thermal shock).

The introduction of lithium oxide as a component in glasses improves the quality of the glass, simplifies the production technology, and facilitates subsequent glass-working. Lithium glasses are extensively used in the production of glass articles for television and radio industries, light-sensitive glasses, glasses which transmit ultraviolet light and absorb infrared light, lithium-borate glasses for X-ray tubes, optical glasses, and electrical insulation glasses.

An important type of lithium-containing vitreous material is the so-called Pyroceram — a vitreous-crystalline material formed in the crystallization of light-sensitive glass (containing 60 to 85% SiO_2, 5.5 to 15% Li_2O, and 2 to 25% Al_2O_3) under shortwave irradiation and after heat treatment. The tensile strength of Pyroceram ranges from 25.3 (for nonpolished) to 14 kg/mm^2 (for polished Pyroceram), its Mohs hardness is 7.5 and its density is 2.5 to 2.6. The thermal expansion coefficient of Pyroceram may be varied within very wide limits and may assume both negative and positive values (up to $20 \cdot 10^{-6}$). The heat conductivity of Pyroceram is three times that of Pyrex glass; it has a high thermal stability and a high softening point (up to 1350°).

Welding and soldering of aluminum, magnesium, nonferrous metals and alloys. Lithium chloride and fluoride are extensively used as flux components for welding and for welding electrodes (use is made here of the low melting point, high boiling point, and good fluxing and deoxidizing properties of the lithium salts).

The introduction of a mixture of lithium, zinc, potassium and sodium chlorides into the joint to be welded makes it possible to weld aluminum to copper, titanium and other metals. A lithium-containing solder is used for the soldering of tungsten to other metals and stainless steel.

Electrical technology. The most important application of lithium in this branch is the use of lithium hydroxide as a component of the electrolyte in alkaline iron-nickel and cadmium-nickel storage batteries; the use of lithium hydroxide increases the capacity of the batteries by 12%, their resistivity by 21%, and their service life by a factor of 2 to 3. In the USSR, either KOH + LiOH or NaOH + LiOH solutions are used as the electrolyte in alkali batteries. Lithium bromide may be used in special delayed action galvanic cells. The addition of lithium chloride or bromide to the zinc and ammonium chlorides in dry cells makes it possible to use cells down to -50°.

Metallurgy. Lithium is extensively used in metallurgy for the deoxidation, alloying and modification (changing to the required structure) of cast iron, various aluminum and magnesium alloys, antifriction and other nonferrous alloys.

Lithium alloys containing 2 to 10% Li and lithium-calcium alloys containing 50 to 70% Ca are commonly used for the deoxidizing and outgassing of metals and alloys. Because of the great affinity of lithium for oxygen, hydrogen, sulfur, nitrogen, and phosphorus, these contaminants

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can be removed from high-carbon-chromium and austenitic steels and from alloys based on copper, copper-silicon, zinc, lead, tin, magnesium, and aluminum. At the same time, the lithium added acts as a modifier which imparts to the metal a fine-grained structure, while the addition of lithium to cast iron removes gaseous inclusions, increases the fluidity and favors the ordered distribution of graphite particles (in particular, it leads to the formation of cast iron with spheroidal graphite).

Lithium is used in antifriction bearing alloys, because of its ability to form (with a number of metals) chemical compounds of relatively high melting points, which are precipitated by suitable heat treatment in the form of very fine particles. These particles wedge the slip planes of the crystallites of the base metal or alloy and improve its hardness, wear-resistance and thermal stability. Lead-lithium alloys possess especially valuable antifriction properties.

The use of lithium salts as components of molten-salt baths for the electrolytic production of metals is of great importance for the manufacturing of some light and rare metals.

Lithium vapors are used for the creation of a reducing and protective atmosphere in furnaces. At the same time the lithium removes moisture, oxygen and nitrogen from the furnace volume and prevents the carbonizing or decarbonizing of the surface layer of metals and alloys during their heat-treatment (annealing).

Other uses. Lithium compounds are used in the chemical industry (hydride, alumohydride, amide) in the synthesis of various organic compounds and as catalysts in the production of polymers (lithium stearate and carbonate); in gas-purification techniques (air conditioning), and in the pharmaceutical, textile and food industries. Lithium hydride and alumohydride are used as sources of hydrogen.

115. LITHIUM MINERALS AND ORES

Lithium is fairly abundant (its concentration in the Earth's crust is 0.0065%) and is one of the lithophylic elements*. Lithium deposits are mostly associated with magmatic rocks.

In addition, lithium has been found in the soil (0.001 to 0.069%), in brines (0.001 to 0.002%), in the sludge from mud volcanos (up to 0.1% Li_2O), in sea water (0.000015%), and in coals, in flora and fauna. The most important commercial deposits consist of granitic pegmatites in which the lithium is associated with sodium, owing to the close energetic characteristics of the ions of these two metals. The presence of lithium in many ferrous-magnesia minerals is due to the closeness of the ionic radii of lithium, Mg^{2+}, Fe^{2+}, and Al^{3+}. In some deposits lithium is associated with fluorine, beryllium, boron, and helium, the last three of which (i.e., the lightest elements) are neighbors of lithium in the periodic table. Most lithium minerals (except alumosilicates of the mica type) are readily modified by weathering, leaching, etc., i.e., processes which lead to a decrease in the lithium content of the surface zone of the deposit.

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* The lithophylic group comprises 54 elements (including the alkali and alkaline-earth metals, aluminum, silicon, etc.) that form silicates, oxides, halides, and salts of the oxygen-containing acids.

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There are up to 150 known lithium-containing minerals, but only two types — silicates and phosphates — are of commercial value. The silicate group comprises the minerals spodumene, lepidolite, zinnwaldite and petalite, and the phosphate group — the double phosphates with aluminum, iron and manganese (lithiophilite and amblygonite).

Spodumene $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ contains 2.9 to 7.6% Li_2O, 20 to 30% Al_2O_3, and 60 to 65% SiO_2 as well as small amounts of Na_2O, CaO, MgO and occasionally Cr_2O_3 (in some cases it contains 0.03 to 0.1% gallium). The mineral has a white-gray color with a greenish or yellowish tinge, a hardness of 6.5 to 7, a density of 3.13 to 3.20, and a melting point of 1380°. It is associated with quartz, felspar, micas, and other components of the granitic pegmatites.

Lepidolite is lithium mica $[(Li, K)(F, OH)] \cdot 3SiO_2 \cdot Al_2O_3$ containing 4.8 to 13.9% K_2O, 1.2 to 4.9% Li_2O, 11.3 to 28.8% Al_2O_3, 46.9 to 60.0% SiO_2, 0.6 to 3.2% H_2O, 1.4 to 8.7% F, and small amounts of MgO, FeO, Cs_2O, and Rb_2O (up to 4%). The mineral is white but it is often colored by contaminants (which impart to it a pink, violet or orange color). Its hardness is 2 to 3, its density is 2.8 to 2.9.

Zinnwaldite $(Li, K)_3Al_3Fe(F, OH)_2Si_{15}O_{16}$ is a lepidolite modification enriched with iron. The mineral has a gray or brown color and a vitreous luster (the cleavage planes have a mother-of-pearl luster). It has a density of 2.9 to 3.2, a hardness of 2 to 3, and a melting point of 945 to 997°. It is encountered together with lepidolite or under the same conditions of occurrence as lepidolite, and is often associated with wolframite, scheelite, cassiterite, fluorite, and quartz.

Petalite is an alumosilicate $Li(AlSi_4O_{10})$ with a lithium oxide content of 3 to 4%. The mineral is gray and occasionally yellowish or pinkish, and has a hardness of 6 to 6.5 and a density of 2.3 to 2.5. It is usually found together with lepidolite, amblygonite, beryl, and pollucite.

Amblygonite $LiAl(PO_4)F$ contains 7 to 10% Li_2O. Its color is white with a yellow, blue or green tinge and it has a hardness of 6 and a density of 2.98 to 3.15.

Spodumene and lepidolite (and to some extent amblygonite and petalite) have a commercial use.

Large reserves of lithium have accumulated in sedimentary deposits. These include some mineral deposits and salt-water lakes in which the lithium accumulates together with sodium, potassium and boron.

Commercial lithium deposits are found in the USSR, Canada, Africa, Brazil, Australia, Spain, Sweden, The German Democratic Republic, and Czechoslovakia. The lithium ore production outside the eastern bloc in 1957 to 1960 was of the order of ~250,000 tons (as a 5% spodumene concentrate).

116. ENRICHMENT OF LITHIUM ORES

The lithium content of ores is small. Thus spodumene ore usually contains 1.5 to 3% LiO_2 while lepidolite contains about 1% Li.

The enrichment of lithium ores is difficult, because of their low lithium content, and the low density and nonmagnetic (or weakly paramagnetic) properties of the lithium minerals.

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Lithium ores are enriched by hand-picking, thermal enrichment (decrepitation), magnetic enrichment, flotation and enrichment in heavy suspensions. In most cases modern enrichment methods employ a combination of several of the above techniques.

Thermal enrichment (decrepitation) is based on the fact that spodumene undergoes a phase transformation (from the α-form with a density of 3.15 to 3.20 to the β-form with a density of 2.44) upon heating to 1000 to 1100°. The 24% increase in volume causes cracking and marked crushing of the mineral.

The ores are crushed to a particle size of -20 to -50 mm and roasted for 1 to 2 hours in a rotary kiln at 1050 to 1100°. The roasting product is then subjected to air-separation or sieving in which the fine spodumene powder is separated from the coarser quartz grains. The enrichment is more difficult in the case of ores containing a large amount of other minerals that also undergo decrepitation (e.g., micas, fluorite, calcite). Moreover, the presence of a large amount of micas causes fusion of the ore at the decrepitation temperature. The decrepitation-enrichment product containing β-spodumene is especially suitable for subsequent processing with sulfuric acid since β-spodumene is readily decomposed by the sulfuric acid.

The flotation of spodumene is carried out with the aid of anionic collectors (fatty acids and their soaps, e.g., oleic acid, aluminum and sodium oleates) in which case the lithium minerals are separated with the foamy product (direct flotation) or with the aid of cationic collectors, in which case the barren rock minerals are separated with the foam product while the lithium minerals remain in the tailings (reverse flotation).

The flotation of lepidolite is carried out mainly with cationic collectors since flotation with fatty acids or their salts requires the advance treatment of the ore with hydrofluoric acid. The cationic collector used is IM-11, which extracts quantitatively the muscovite and separates it from the lepidolite.

TABLE 67

Typical chemical composition of lithium concentrates, %

Components	Concentrate			Components	Concentrate		
	spodumene	amblygonite	lepidolite		spodumene	amblygonite	lepidolite
Li_2O	6.78	8.48	4.65	FeO	0.53	0.02	0.19
SiO_2	62.21	5.16	52.89	MgO	0.13	Traces	0.31
Al_2O_3	28.42	22.76	22.77	CaO	0.11	0.15	0.52
P_2O_5	—	54.42	—	MnO	—	—	0.59
K_2O	0.69	0.30	10.33	F	—	2.67	3.68
Na_2O	0.46	1.63	0.13				

Zinnwaldite is also enriched by flotation; however, since its ores also contain wolframite and cassiterite, they are enriched first by gravitation (on sedimentation machines and concentration tables) followed by magnetic separation of the collective tin-tungsten concentrate. The tailings containing the zinnwaldite are subjected to flotation with the aid of an

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ammoniacal collector (the so-called "kateksol" [sic], a higher fatty acid product) or with technical soap, with the simultaneous use of water glass for the depression of the quartz.

Enrichment in heavy suspensions. The difference between the densities of the lithium minerals and the minerals of the bare rock (quartz, felspar) is only 0.2 to 0.5, i.e., it is not large enough to permit separation by sedimentation or on concentration tables, but it makes it possible to effect separation in heavy suspensions. In the last process, the ground ore is immersed in a suspension of a given density; the ore particles of lower density flow to the surface while the particles of greater density settle on the bottom. Either ferrosilicon or magnetite are commonly used as the suspensoid in the enrichment of spodumene ores by the above method.

Magnetic separation is used as a finishing operation for the separation of magnetic minerals, and also in the enrichment of zinnwaldite ores (zinnwaldite is weakly magnetic).

The approximate composition of lithium concentrates is shown in Table 67.

117. PROCESSING OF LITHIUM CONCENTRATES

The commercial products of the processing of lithium concentrates are lithium salts (LiCl, Li_2CO_3, Li_2SO_4) and lithium hydroxide.

The first stage in the processing involves the decomposition of the concentrates, which may be accomplished by several methods. The most important methods are: decomposition with sulfuric acid, with lime, and the sulfate process. The chlorination-roasting method is also used occasionally.

The sulfuric acid method

The method is based on the reaction between sulfuric acid and β-spodumene (there is virtually no interaction between α-spodumene and sulfuric acid) in which the hydrogen of the acid is substituted for the lithium without a change in the structure of the mineral:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + H_2SO_4 \rightarrow Li_2SO_4 + H_2O \cdot Al_2O_3 \cdot 4SiO_2.$$

The flow sheet for the spodumene decomposition process is shown in Figure 218. After the enrichment (by decrepitation) the cooled and crushed (in a roller mill, to a particle size of -0.074 mm) material is fed to a horizontal screw-conveyer or rollers in which it is mixed with concentrated (93%) sulfuric acid by a sprinkling technique. The sulfuric acid is taken in a 35 to 40% excess above the stoichiometric amount needed (225 kg/ton of concentrate). The sulfatizing is carried out for 10 minutes in a rotary kiln at 250°.

The sinter formed is cooled and leached with water to extract the Li_2SO_4. At the same time chalk is fed to the same reactor (with continuous stirring by means of compressed air) in order to neutralize the excess sulfuric acid to pH 6.0 to 6.5. The solution is separated by filtration on a drum-type vacuum filter and the magnesium and calcium are removed from the

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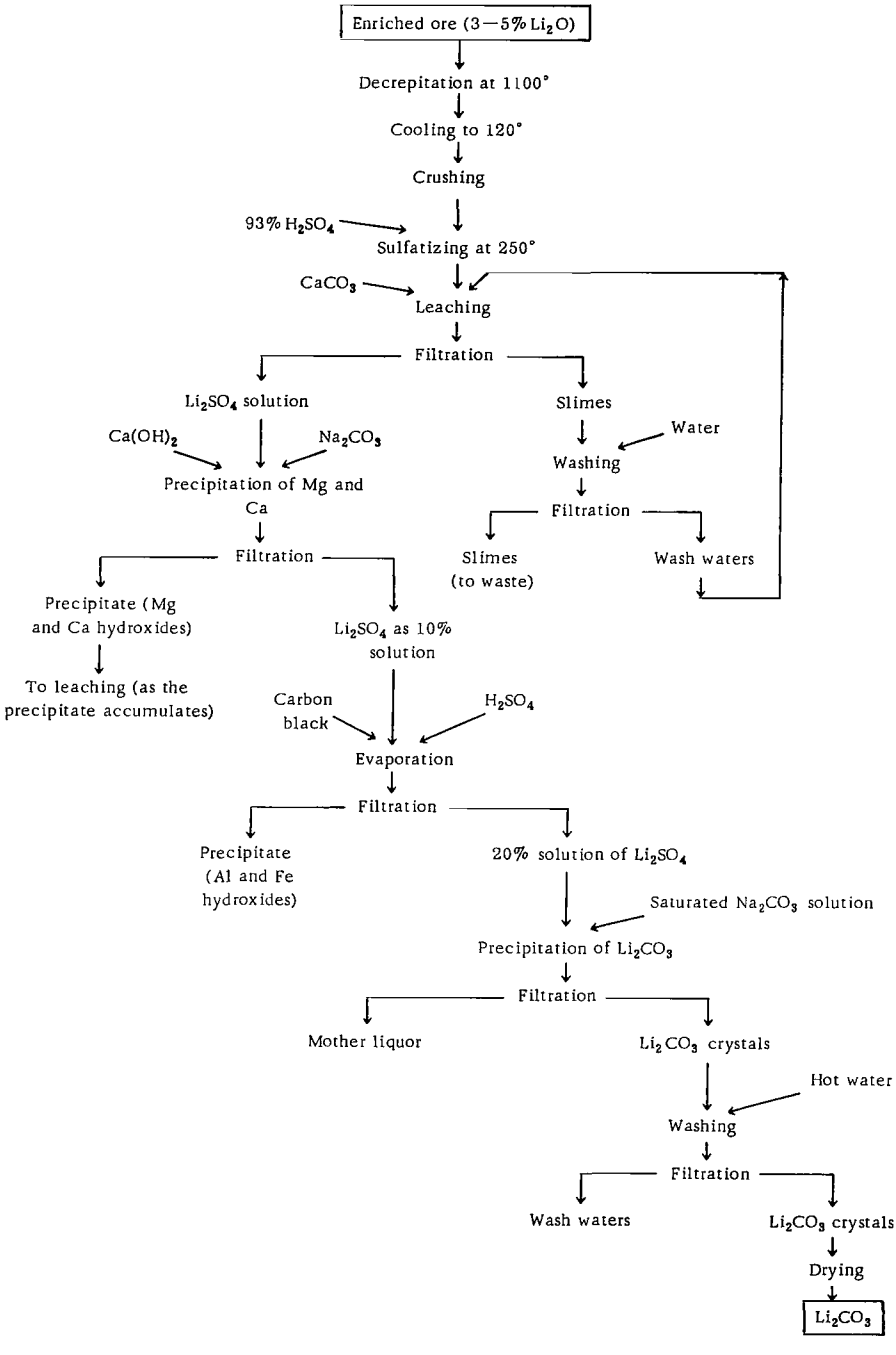

FIGURE 218. Flow sheet for the processing of spodumene by the sulfuric acid method (USA).

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solution by precipitation, respectively, as magnesium hydroxide (by neutralizing the solution with lime, to pH 12 to 14) and calcium carbonate (by treating the solution with sodium carbonate). The remaining solution contains up to 100 g Li_2SO_4 per liter and is contaminated with aluminum (from the ore) and iron (dissolved out of the steel piping). The iron and aluminum are precipitated as the hydroxides by adding sulfuric acid to the solution (to pH 7) together with a small amount of carbon black (which absorbs contaminants present in trace amounts). The solution is then evaporated to a Li_2SO_4 content of 200 g/liter, and the iron and aluminum hydroxides are precipitated simultaneously. The solution is filtered (using a plate and frame-filter press) and lithium carbonate is precipitated by the addition of a saturated solution of sodium carbonate. The lithium carbonate is washed twice with deionized water yielding a product with a carbonate content of 96 to 97%. The precipitate is separated by centrifuging, and dried at a reduced pressure (510 to 635 mm Hg). The dry lithium carbonate is contaminated with sulfate ions, chloride ions, the oxides of sodium, potassium, iron, calcium, and the heavy metals, and contains 0.01% moisture.

Lepidolite is also decomposed with sulfuric acid. In one of the methods, the lepidolite is crushed to a particle size of -0.1 mm, mixed in a steel reactor with concentrated acid at a weight ratio of 1 : 1.1, and the mixture is heated as follows: for 3 hours at 120°, for 1 hour at 136°, for 1.5 hours at 156°, for 1.5 hours at 194°, for 1 hour at 200° and for 0.5 hour at 340°. The sulfatizing leads to the production of silica and of lithium, aluminum, potassium, sodium, rubidium, and cesium sulfates. The overall process is expressed by the equation:

$$3SiO_2 \cdot Al_2O_3 \cdot 2[(Li, K)(F, OH)] + H_2SO_4 \rightarrow$$
$$\rightarrow Li_2SO_4 + Al_2(SO_4)_3 + K_2SO_4 + H_2SiO_3 + SiF_4 + H_2O.$$

The reaction mass is allowed to cool, treated with water, the solution (containing the sulfates) is filtered and the bulk of the aluminum is removed as alums. The alums are formed by adding potassium sulfate to the solution:

$$Al_2(SO_4)_3 + K_2SO_4 = 2K[Al(SO_4)_2].$$

The solubility of alum increases sharply with increasing temperature:

Temperature, °C	0	15	30	60	100
Solubility, g/100 g water	3.0	5.0	8.4	24.8	154

Hence, the alum is separated by crystallization at -5 to 0°.

For the quantitative separation of the aluminum, the solution is neutralized with chalk and freshly precipitated aluminum hydroxide is added; this leads to the precipitation of the aluminum together with the potassium as $K_2SO_4 \cdot 3Al_2O_3 \cdot SiO_2$ and of gypsum. The solution containing the Li_2SO_4 contaminated with iron, manganese, and other ions is evaporated and purified by the addition of milk of lime; the iron and manganese are precipitated as the hydroxides.

A concentrated solution of sodium or potassium carbonate is added to the purified solution, causing precipitation of lithium carbonate, which is washed and dried at 60°. The mother liquor containing K_2SO_4 is returned to the precipitation of aluminum-potassium alum.

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The lime method

The lime method for the decomposition of lithium-containing concentrates is based on the roasting of the concentrate with lime or limestone, followed by leaching of the sintered mass with water. The roasting of spodumene with lime leads to the formation of lithium aluminate and calcium silicate:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + 8CaO \rightarrow Li_2O \cdot Al_2O_3 + 4(2CaO \cdot SiO_2),$$

while the lithium aluminate reacts during the leaching with the excess calcium oxide yielding the hydroxide:

$$Li_2O \cdot Al_2O_3 + Ca(OH)_2 \rightarrow 2LiOH + CaO \cdot Al_2O_3.$$

During the roasting, a large excess of calcium oxide is required for the formation of soluble lithium hydroxide; the optimum concentration of the calcium oxide in the charge is 75% (Figure 219). Sodium and potassium aluminates are also formed during the roasting; by analogy with lithium aluminate, these two aluminates also react with the lime and are converted to the respective hydroxides.

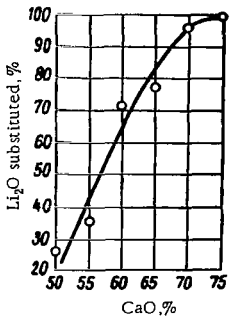

FIGURE 219. Substitution of Li_2O in spodumene at 1000° as a function of the calcium oxide concentration in the reaction mixture.

A sample flow sheet for the processing of spodumene by the lime method is shown in Figure 220. The concentrate and the limestone are ground in a wet mill to a particle size of -0.074 mm, mixed, and the pulp is thickened to a solid content of 65%. The roasting is carried out in a rotary furnace at 1150 to 1200°, the sinter is ground to a particle size of -0.147 mm, leached at a solid : liquid ratio of 1 : 3, and the sands from the first leaching are washed in five thickeners in series; the overflow liquids from the thickeners are returned to the wet-milling of the sinter and the leaching operations. The lithium hydroxide solution from the first thickening is taken for evaporation and for the crystallization of the $LiOH \cdot H_2O$. The crystals are separated by filtration in a centrifuge and the product ($LiOH \cdot H_2O$) containing 30% of moisture is dehydrated in a drum drier. The mother liquor from the centrifuging is returned to the crystallization. Sodium and potassium aluminates, sodium and potassium hydroxides, and rubidium and cesium accumulate gradually in the mother liquor. When the mother liquor is contaminated it is withdrawn from the process cycle and taken for regeneration.

A variant of the alkaline method involves the decomposition of spodumene by processing with milk of lime under pressure. The ground spodumene concentrate is mixed with lime at a weight ratio of 100 : 193 and treated with water for 2 hours at 190 to 200° (with mixing). The reaction between the spodumene concentrate and the lime leads to the formation of lithium hydroxide, aluminum hydroxide, and calcium silicate:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + CaO + H_2O \rightarrow LiOH + CaSiO_3 + Al(OH)_3.*$$

The Na_2O originally present in the concentrate as an impurity is dissolved and the Na_2O concentration in the solution reaches up to 1 to 4%.

The silica remains almost quantitatively in the solid residue; the aluminum is partially dissolved as the aluminate $NaAlO_2$. In some cases the small amounts of calcium and aluminum dissolved in the

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* [sic.]

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process are precipitated by carbonation (passing a stream of CO_2 or furnace gases) of the LiOH-containing filtrate; this causes neutralization of the alkali.

The aluminate is hydrolyzed as a result of the sharp decrease in the alkalinity of the solution, and aluminum hydroxide is precipitated:

$$NaAlO_2 + 2H_2O = Al(OH)_3 + NaOH.$$

The hydroxide formed reacts with CO_2 yielding sodium carbonate and causing almost quantitative hydrolysis of the aluminate and precipitation of the aluminum. The calcium is precipitated as $CaCO_3$. Lithium carbonate is obtained by evaporation and a second carbonation.

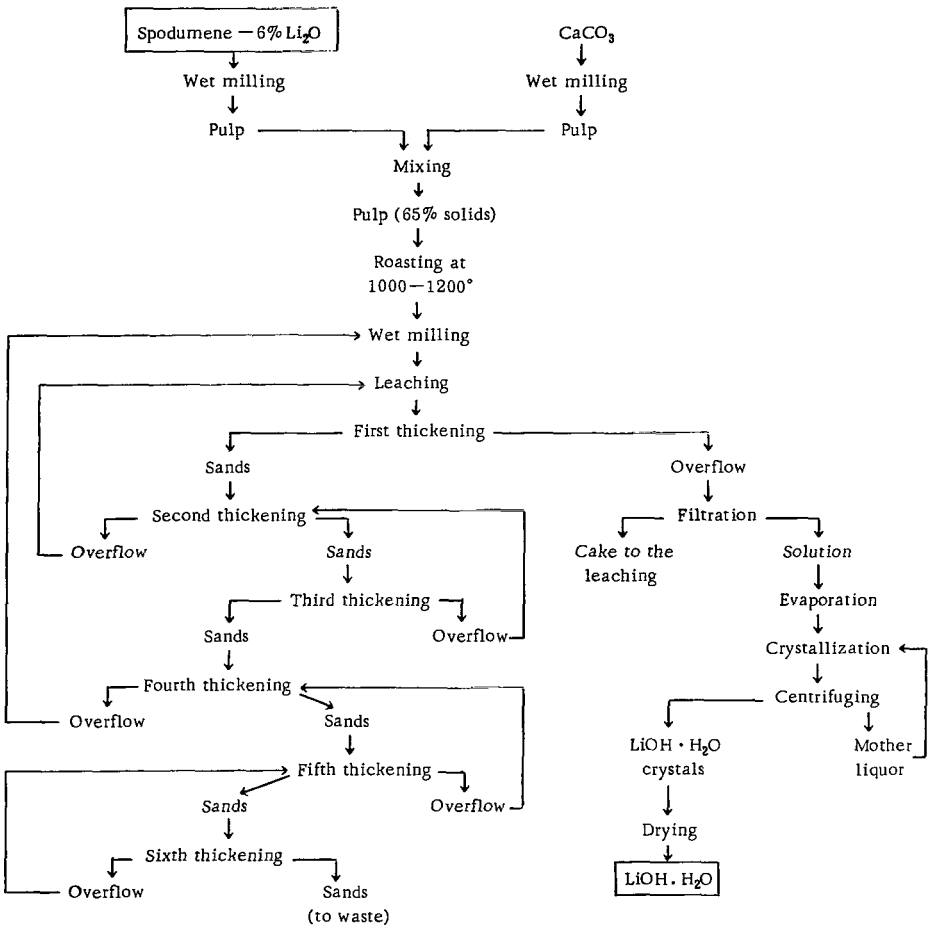

FIGURE 220. Flow sheet for the processing of spodumene by roasting with lime (USA).

The lime method has the advantages of being universally adaptable, of using cheap reagents, and of yielding wastes (silicate-containing slimes, calcium aluminate, chalk) that may be used in the production of structural binding materials.

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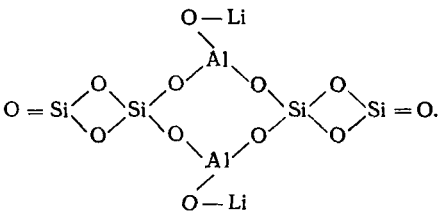
The sulfate method

The method involves the sintering of spodumene with potassium sulfate. The decomposition with potassium sulfate is based on the displacement (substitution) of lithium in the spodumene by potassium:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + K_2SO_4 = Li_2SO_4 + K_2O \cdot Al_2O_3 \cdot 4SiO_2.$$

According to Vernadskii the structure of spodumene may be represented as:



The position of the lithium atoms explains the relative ease with which they are replaced by the atoms of other alkali metals and especially potassium. However, potassium atoms are larger than lithium atoms, hence the substitution of potassium for lithium is possible only if the atomic bonds in the spodumene crystal lattice are weakened, i. e., at elevated temperatures.

According to Plyushchev, the reaction between spodumene and potassium sulfate and the liberation of lithium as a water-soluble substance starts even before the fusion of the reaction mixture, i. e., at $\sim 700°$, and involves a solid-phase reaction which passes through the stage of formation of a potassium-sodium leucite (K, Na) Al[Si_2O_6], sodium-potassium alumosilicate which is sparingly soluble in water.

In practice, the sintering is carried out at 920 to 1150°. During the sintering α-spodumene is converted into β-spodumene which enters a substitution reaction with the K_2SO_4:

$$\underset{\alpha\text{-spodumene}}{(Li,\ Na)\,Al[Si_2O_6]} \rightarrow \underset{\beta\text{-spodumene}}{(Li,\ Na)\,Al[Si_2O_6]},$$

$$2\underset{\beta\text{-spodumene}}{(Li,\ Na)\,Al[Si_2O_6]} + K_2SO_4 \rightleftarrows \underset{\alpha\text{-leucite}}{(K,\ Na)\,Al[Si_2O_6]} + LiSO_4.$$

α-leucite is converted into β-leucite with the evolution of heat.

Since the decomposition of spodumene with potassium sulfate is a reversible reaction, a large excess of the sulfate is required to shift the reaction to the side of lithium sulfate formation. Sodium sulfate may be substituted for part of the potassium sulfate.

One variant of the sulfate method for spodumene decomposition is shown in Figure 221. The spodumene ore is enriched by decrepitation, the spodumene fraction is separated by sieving from the coarser quartz fraction, and the spodumene fraction is mixed with an excess of potassium sulfate, at a weight ratio of 1 :(0.6 to 1.1). The reaction mixture is

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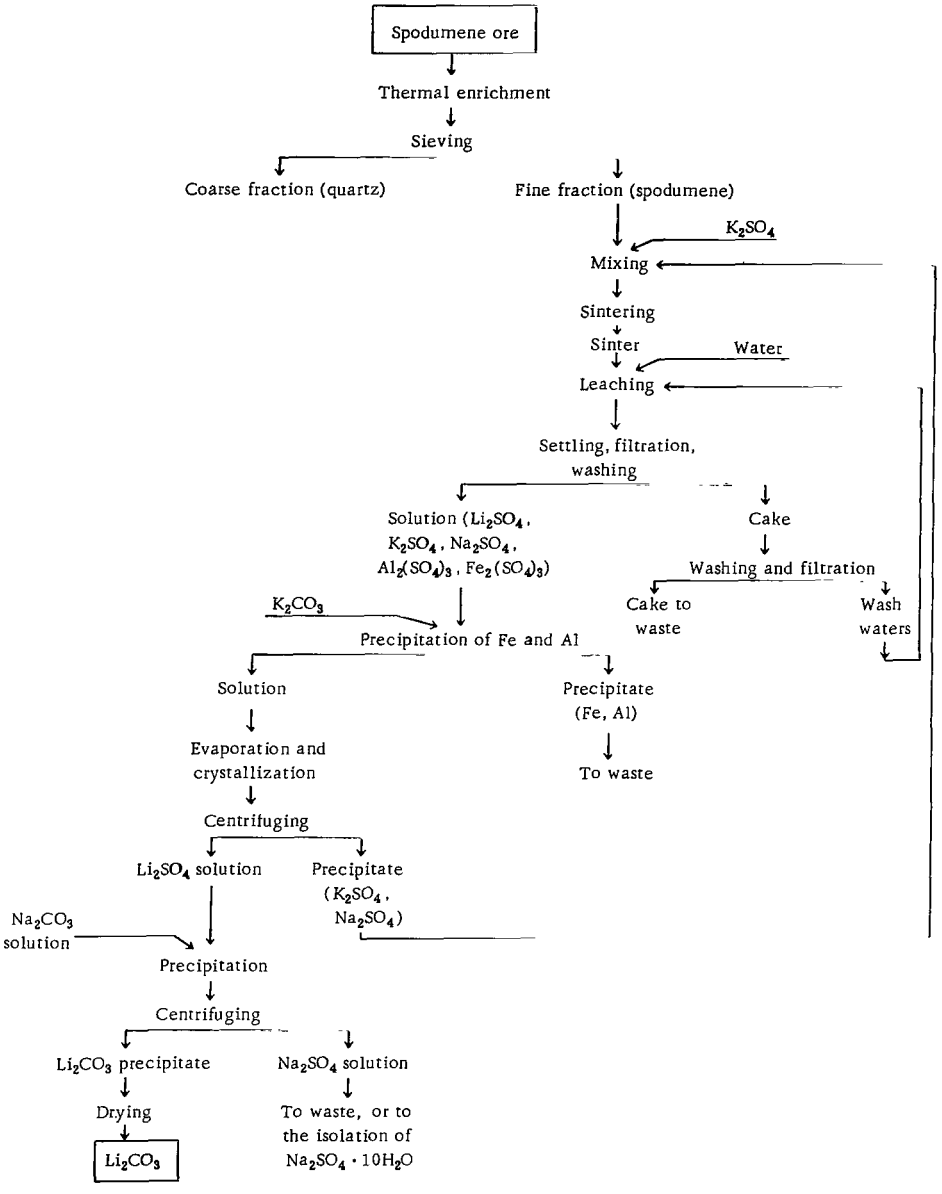

FIGURE 221. Flow sheet for the processing of spodumene by sintering with potassium sulfate.

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sintered by heating for 2 hours at 1100 to 1150°, usually in a rotary kiln. The sinter is leached with cold water, since the solubility of Li_2SO_4 decreases with increasing temperature. The solution is separated from the solid residue by decantation or by settling and filtration, the cake (consisting almost exclusively of sodium-potassium alumosilicate) is discarded, and the solution containing Li_2SO_4 as well as K_2SO_4 and small amounts of Na_2SO_4, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ is treated with a solution of potassium carbonate, which causes precipitation of the aluminum and iron as the hydroxides. After filtration, the solution contains lithium, potassium and sodium sulfates; the solution is evaporated, causing the precipitation of most of the potassium sulfate (together with the Na_2SO_4), which is separated by centrifuging. The potassium sulfate is returned to the process, while the solution is heated to 80 to 90° and the sparingly soluble lithium carbonate is precipitated by the addition of a sodium carbonate solution.

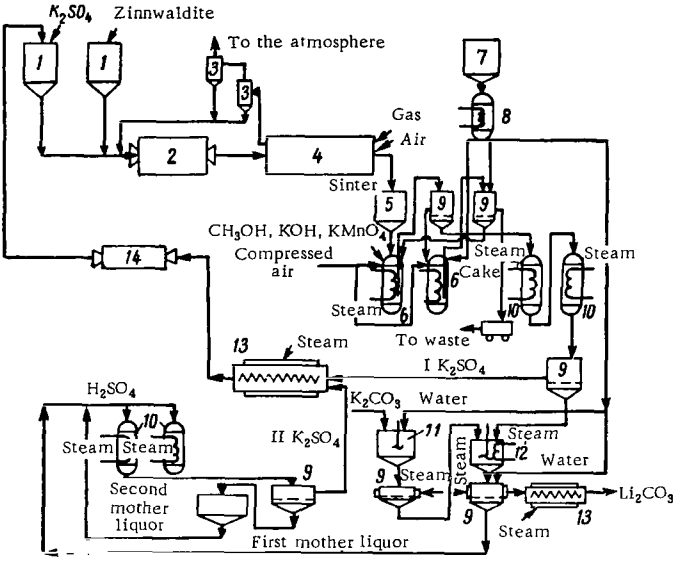

FIGURE 222. Flow sheet of the processing of zinnwaldite by sintering with potassium sulfate (Czechoslovakia).

1—bins; 2—mixer-grinder; 3—dust collectors; 4—roasting rotary kiln with direct heating; 5—intermediate bin; 6—reactor, for the leaching of the sinter; 7—distilled water storage tank; 8—heater; 9—suction filter; 10—evaporators; 11—reactor, for the preparation of the saturated potassium carbonate solution; 12—reactor, for the precipitation of lithium carbonate; 13—drying furnace; 14—mill, for the grinding of the recovered potassium sulfate.

In Czechoslovakia the sulfate method is used for the processing of a lithium-containing mineral by the scheme shown in Figure 222. A mixture of zinnwaldite enriched by flotation (approximate composition: 2.7% Li_2O, 10.8% K_2O, 46.6% SiO_2, 6.7% F, 7.9% FeO, 23.0% Al_2O_3, 1.7% MnO) and

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potassium sulfate, at a weight-ratio of 10 : 3.5 is sintered at 900°. The sinter is leached with water and the lithium (up to 90 to 95% of the amount initially present) and all the soluble sulfates are extracted. In order to precipitate the iron and alumonium hydroxides, potassium permanganate is added to the solution (to oxidize Fe^{2+} to Fe^{3+}) and the solution is made alkaline by the addition of KOH. The excess oxidizing agent is reduced with methanol to MnO_2, which is separated together with the insoluble residue. The mixture is separated by filtration and the filtrate is concentrated to a lithium content of 10 g/l. Potassium sulfate is precipitated during the concentration; this precipitation is aided by the addition of KCl as a salting-out agent. The potassium sulfate is separated and the solution is treated with a saturated solution of potassium carbonate, causing the precipitation of lithium carbonate, which is separated by centrifuging; the mother liquor contains up to 40% of the initial amount of lithium. The evaporation of the mother liquor is repeated, causing crystallization of a mixture of potassium and lithium sulfates which is dried, crushed, and returned to the sintering stage. The mother liquor is returned to the evaporation of the basic solutions. The total degree of extraction of lithium in the final product is 90%, and the final product contains $\geqslant$ 97% lithium carbonate.

Chlorination roasting

Chlorination roasting involves the sintering of spodumene with chlorinating agents (NH_4Cl, $CaCl_2$).

In a method developed by Sobolev the spodumene concentrate is sintered with chalk and ammonium chloride (as a 1 : 3 : 1 mixture) (see Figure 223). The sintering is carried out in a hearth or rotary furnace first at 250 and then at 750°. This causes decomposition of the mineral and formation of lithium chloride:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + 4CaCO_3 + 2NH_4Cl = 2LiCl + 4CaSiO_3 + Al_2O_3 + 4CO_2 + 2NH_3 + H_2O.$$

The sinter contains up to 97 to 98% of the lithium, the rest is lost by entrainment with the dust during the sintering.

The sinter is leached with cold water. The leach liquor containing the LiCl and $CaCl_2$ is separated by filtration from the silicate residue. The solution is evaporated, leading to the crystallization of a mixture of lithium and calcium chlorides, which may be used directly for the electrolytic production of lithium.

In order to obtain lithium oxide from the chloride solution, the lithium and calcium are precipitated as the carbonates by the addition of an excess (125%) of ammonium carbonate. The precipitate is treated with milk of lime, this leads to the dissolution of the lithium as hydroxide:

$$Li_2CO_3 + Ca(OH)_2 = 2LiOH + CaCO_3.$$

The solution is evaporated and the lithium hydroxide is crystallized (as $LiOH \cdot H_2O$).

Pure lithium chloride is occasionally prepared from the solution containing sodium, lithium, potassium and calcium chlorides. To this

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end, a current of dry hydrogen chloride is passed through the solution. All the chlorides are precipitated, while the lithium chloride which remains in the solution is crystallized (by evaporation) as $LiCl \cdot H_2O$. The lithium chloride is dehydrated and taken for electrolysis, for the preparation of lithium metal.

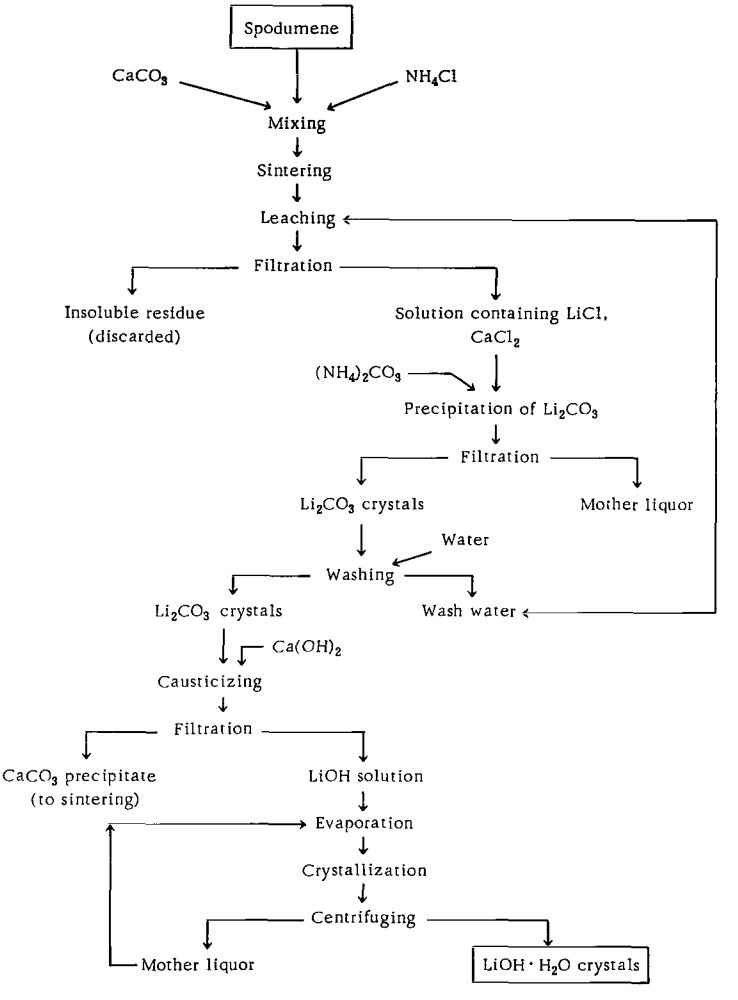

FIGURE 223. Flow sheet for the processing of spodumene by decomposition with chalk and ammonium chloride.

Another variant involves the sintering of spodumene with $CaCO_3$ and $CaCl_2$ at 1150 to 1200°; the lithium chloride formed is volatilized (it volatilizes at about 1000°) and is collected in dry or wet condensers together with the dust. In the wet process, the lithium chloride vapor coming from the reactor as a mixture with the dust-containing gases is separated from the dust, washed with a large amount of water,

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and the dilute solution formed is filtered. The filter residue is returned to the roasting kiln. The solution is evaporated to a LiCl concentration of 40%, the NaCl precipitate is removed, the solution is cooled, and the crystallized KCl is separated. The lithium is then precipitated from the solution as the carbonate. In the dry method, the lithium chloride is extracted from the dust with the aid of organic reagents.

The chlorination roasting makes it possible to obtain pure LiCl directly from the ore at a yield of $\geqslant 90\%$; however, some difficulties are associated with the collection of the lithium chloride and with the high corrosiveness of the furnace gases — a fact that makes it necessary to use expensive materials for the equipment which, nevertheless, has a short service life.

118. PRODUCTION OF LITHIUM

The main commercial method for the production of lithium involves the electrolysis of lithium chloride in a molten medium. Methods based on thermal reduction with metals have also been used recently. These methods are also used for the production of lithium alloys.

Production of lithium by electrolysis of molten salts

The commercial method for the production of lithium by electrolysis of molten salts was developed in 1932 to 1934 in the USSR, by Izgaryshev, Pletenov and Ivanova.

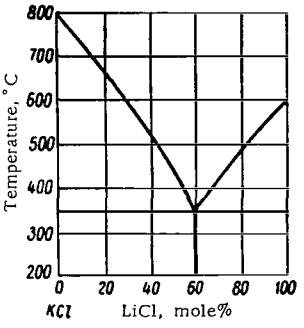

FIGURE 224. Phase diagram of the system LiCl—KCl.

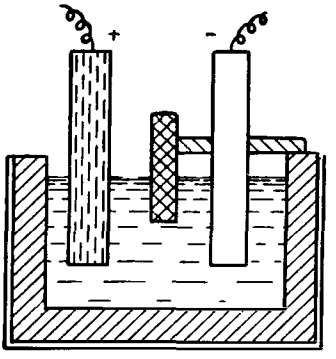

FIGURE 225. Diagram of a bath for the electrolytic production of lithium.

The electrolysis is carried out in a LiCl + KCl mixture (1 : 1 by weight), whose composition is close to that of the eutectic mixture (the eutectic mixture contains 60 mole% LiCl and melts at 352° (see Figure 224).

The anhydrous lithium chloride required for the electrolysis is prepared by dissolving pure lithium carbonate in hydrochloric acid. The solution is evaporated in equipment made of special alloys, and the chloride is crystallized as $LiCl \cdot H_2O$. The chloride is dehydrated at 120 to 150°.

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The USSR specifications for the maximum impurity content of LiCl are as follows: 0.12% Na, 0.03% Ca, 0.05% Al, 0.005% Fe, 0.1% SO_4^{2-}, 0.05% SiO_2, 0.005% PO_4^{3-}.

A diagram of a bath used in the electrolytic production of lithium is shown in Figure 225. The bath consists of a steel jacket (wall thickness 4 to 5 mm) lined with talcum stone or magnesite; the anodic space is separated from the cathodic space by an alundum (Al_2O_3) partition that does not reach the bottom of the electrolyzer. The ratio of the anodic to cathodic space volumes is 1 : 2. A graphite anode and an iron rod cathode are used. The cathodic current density is 5 amp/cm^2. The chlorine gas is removed by means of an exhaust fitted in the anodic space. Fresh lithium chloride is added periodically to the anodic space to replace the lithium chloride consumed during the electrolysis. The lithium metal formed in the electrolysis flows to the surface of the molten electrolyte and collects under the cover of the cathodic space. The lithium is scooped from the cathodic space and cast into ingots. The electrolysis is carried out at 400 to 430°. The current efficiency is about 75%, and the consumption of electrical energy is 55 to 60 kwh/kg lithium. The metal produced contains at least 98% lithium, the main impurities being sodium, magnesium (up to 1%), iron (up to 0.04%), potassium (0.01 to 0.05%), and silicon (0.02 to 0.05%). The magnesium, silicon, and sodium enter the metal from the talcum-stone lining; the sodium content depends on the purity of the lithium chloride while the potassium content depends on the conditions of the electrolysis. Increasing the potassium chloride concentration in the electrolyte leads to an increase in the potassium concentration in the lithium, to 2 to 3%. It should be mentioned that the decomposition potentials of the potassium and lithium chlorides have similar values (i. e., at 405° the difference between them is only 0.112 V), hence, it is not possible to prepare potassium-free lithium by electrolysis of a eutectic mixture of the chlorides.

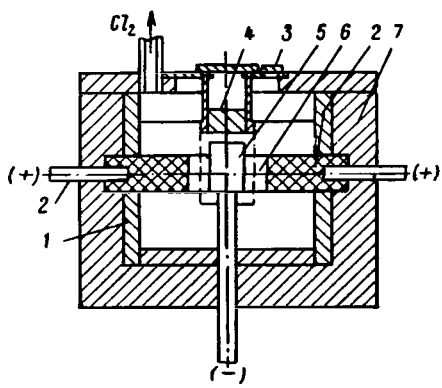

FIGURE 226. Diagram of a bath for the electrolytic production of lithium (West Germany).

1—bath lining; 2—anode; 3—opening for the introduction of the salts; 4—liquid lithium; 5—cathode; 6—diaphragm; 7—body of electrolyzer.

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An electrolyzer used for the production of lithium at the Degussa-Rheinfelden plant (West Germany) is shown in Figure 226. On the exterior the bath is lined with refractory bricks, and the internal lining consists of a dense layer of talcum or alundum about 50 mm thick. The top of the bath is made of the same material, of the same thickness, and has a round opening at its center (100 mm in diameter, serving for the collection of the metal), and openings for the charging of the raw materials and for the evacuation of the chlorine. The lithium-collecting device has a cylindrical shape with a cupola-shaped tip, which facilitates the collection of the fine lithium particles as they float on the surface of the melt. The tip of the collecting device is fitted with an iron-wire partition for the separation of the free chlorine from the metallic lithium.

The anode consists of 3 graphite plates (150 × 600 × 70 mm) and six graphite rods with a screw thread for the connection of the anodes to the electrical bus bars. A vertical steel rod 50 mm in diameter, which is connected to a tubular refractory-steel casting 102 mm in diameter, serves as the cathode. The rod passes through the hollow of the steel casting, which is fastened to the bottom of the bath; the electrical contact to the cathode is accomplished by means of copper clamps and a cable which is connected to a bus bar passing beneath the floor.

The lithium chloride taken for the electrolysis (containing 94 to 98% LiCl, 2.5% KCl, 1.5% NaCl, 0.5% Fe_2O_3) is melted in advance and ground. The mixture taken for electrolysis contains 52% lithium chloride and 48% potassium chloride. The electrolyte is molten in advance in a 500 kg crucible, maintained for 6 to 7 hours at 390°, analyzed, and then kept for another 5 hours under these conditions. The molten electrolyte is poured into the preheated electrolysis bath, and the current is switched on. Fresh 2.5 kg portions of lithium chloride are added to the bath each ~ 2 hours.

The lithium formed in the electrolysis flows to the upper part of the collecting device, where it is stored under a layer of oil (of high boiling point). The metal is periodically withdrawn with the aid of a perforated ladle (made of thin iron wire); the metal remains in the ladle while the oil passes through the openings, except for a small amount that remains in the ladle and protects the lithium during the transfer to the collecting vessel.

The daily production of each bath is 4 to 5 kg of lithium, containing (after remelting) 97% lithium and small amounts of potassium and sodium. The current efficiency is 83%, the specific consumption of electrical energy is 144 kwh/kg.

Lithium of a higher degree of purity is prepared in baths lined with graphite. Very pure lithium (containing 0.4 to 0.7% Na, 0.01% K, 0.02% Ca, 0.001% Fe, and 0.06% N) may be prepared in these baths by using pure lithium chloride. The current efficiency with such baths reaches up to 90% and the yield of lithium is 95%.

In order to remove occluded electrolyte and oxides from the electrolytic lithium it is remelted under a layer of vaseline oil or paraffin, in steel or zirconia crucibles lined with lithium fluoride (which resists the effect of molten lithium up to 800°).

In order to prevent oxidation, lithium metal is stored (in the shape of rods, wire, or ingots) in a hermetically sealed vessel under an inert liquid (e.g., mineral oils, paraffin, kerosene). Lithium products may also be coated with a layer of paraffin, for instance by passing lithium

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rods through a molten paraffin bath. Recently, lithium products have been stored by pressing in thin aluminum or copper shells; this simplifies the handling of lithium since fragments of the required length may be cut before use.

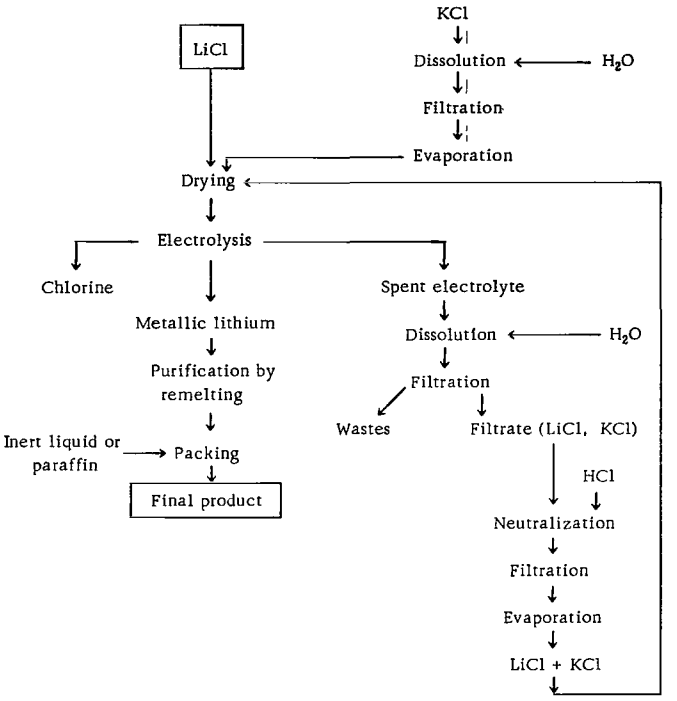

FIGURE 227. Flow sheet for the electrolytic production of lithium.

The spent electrolyte consists of a mixture of KCl and LiCl contaminated with graphite dust (formed as a result of the decomposition of the anode and the bath lining if this is made of graphite). This mixture is processed for the recovery of the lithium chloride, which is returned to the electrolysis as shown in Figure 227. The salt mixture is leached with water in iron reactor. The solution is strongly alkaline, owing to the interaction between the metallic lithium occluded in the electrolyte and the water; it is neutralized with hydrochloric acid to a weakly acid reaction and is evaporated to crystallize the LiCl + KCl mixture. In practice, this mixture contains up to 60% LiCl. The composition is adjusted and the mixture is returned to the electrolysis.

The electrolysis of molten salts may also be used for the preparation of binary lithium alloys, by using in the electrolysis a mixture of lithium chloride and the second component of by using a liquid metal cathode.

Production of lithium by thermal reduction with metals

In spite of the fact that the commercial production of lithium by electrolysis of molten salts is a successful process, considerable difficulties are involved in the design of equipment for the production of pure lithium chloride (because of its high chemical reactivity), and because of the unavoidable contamination of the lithium with sodium and some other elements.

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In order to eliminate these difficulties, a study was made of methods for the production of lithium by thermal reduction with metals, and such methods are used occasionally. They are based on the reduction of lithium oxide, carbonate, or fluoride or the direct reduction of spodumene with aluminum, silicon, or magnesium (in a vacuum).

Reduction of lithium oxide. The reduction of lithium oxide may be represented by means of the following equations:

$$3Li_2O + 2Al = 6Li + Al_2O_3 - 33.6 \text{ kcal},$$
$$2Li_2O + Si = 4Li + SiO_2 - 76.3 \text{ kcal};$$
$$Li_2O + Mg = 2Li + MgO + 3.8 \text{ kcal}.$$

Thus, the reduction of lithium oxide is either endothermic or slightly exothermic. Thus, it can be carried out only in a vacuum, where the high evaporation pressure of the metallic lithium shifts the reaction to the right-hand side and ensures its completion. In addition, lithium produced in a vacuum is purified and protected against oxidation during the process.

Oxides of the reducing agents used are formed during the reduction, and they combine with the lithium oxide yielding aluminates, silicates, etc. In order to prevent this reaction, the charge taken contains calcium oxide which combines with the Al_2O_3 or SiO_2 to yield the monoaluminate or silicate respectively:

$$2Li_2O + 2CaO + Si = 4Li \text{ (vapor)} + Ca_2SiO_4;$$
$$3Li_2O + CaO + 2Al = Li \text{ (vapor)} + CaO \cdot Al_2O_3.$$

The lithium oxide used in thermal reduction with metals is produced by roasting lithium hydroxide or carbonate at 800°.

The thermal reduction process is carried out as follows. The LiO_2 is mixed with the CaO, the mixture is roasted, crushed, and mixed with the ground (to ~0.15 mm) reducing agent—silicon or aluminum powder, which is taken in a ~ 10% excess above the stoichiometric amount needed; the mixture is pelletized and transferred to a vacuum furnace which is diagrammatically shown in Figure 228. The working space of the furnace is connected to a condenser, a diffusion pump and a rotary (oil) vacuum pump. The furnace is heated with the aid of heaters positioned in a tubular muffle, and the temperature is controlled by means of a thermocouple and a galvanometer. The residual pressure in the system prior to the beginning of the reduction process is 10^{-3} mm Hg. The degree of extraction of lithium during the reduction with silicon (at 1300°) is 92 to 93%, while in the reduction with aluminum (at 900°) it is of the order of 80%.

The reduction of lithium oxide with magnesium is not satisfactory because of the high vapor pressure of magnesium (the melting points of magnesium and lithium are 1100 and 1327° respectively) which accompanies the lithium in the distillate; the degree of extraction of the lithium with the lithium-magnesium distillate formed at 950° does not exceed 73%.

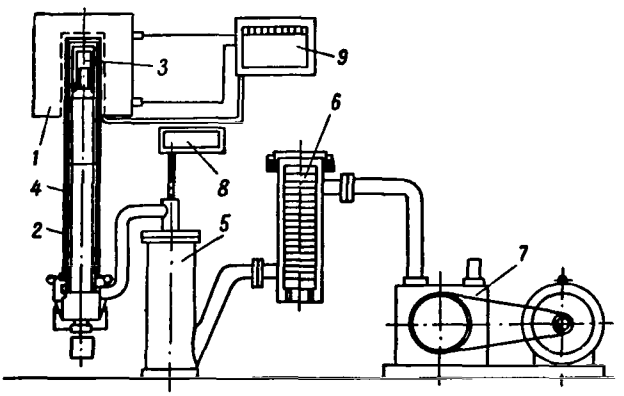

FIGURE 228. Diagram of an apparatus for the production of lithium by thermal reduction in vacuo.

1—furnace; 2—retort; 3—working space of the furnace; 4—condenser; 5—diffusion pump; 6—trap; 7—rotary pump; 8—vacuum measuring gauge; 9—potentiometer (for temperature measurements).

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Reduction of lithium halides. Because of its great volatility, LiCl cannot be reduced to lithium by a vacuum-thermal method; hence, lithium fluoride LiF (which at 1390° has a vapor pressure of about 81 mm Hg) is taken for the reduction. The lithium fluoride is mixed with aluminum or silicon and calcium oxide. In this case the calcium oxide is added not only in order to bind the Al_2O_3 or SiO_3 formed in the process (to calcium aluminate or silicate respectively) but also in order to bind the fluorine as calcium fluoride. The formation of calcium fluoride prevents volatilization of the aluminum and silicon (as AlF_3 and SiF_4) together with the lithium vapor.

The following reactions occur when the charge is heated in a vacuum:

$$6LiF + 4CaO + 2Al = 6Li + Ai_2O_3 \cdot CaO + 3CaF_2,$$
$$4LiF + 3CaO + Si = 4Li + CaO \cdot SiO_2 + 2CaF_2.$$

The condensate from the thermal reduction with aluminum (which is carried out at 1000°) contains about 90% metallic lithium, the rest being lithium fluoride; the yield of lithium passing into the condensate is 44 to 45%; the lithium yield in thermal reduction with silicon (which is carried out at 1100°) is only 22 to 23%.

Reduction of lithium aluminate. The research of Kiselev has shown that high-purity lithium may be prepared by reduction of lithium aluminate with aluminum; a lithium yield of over 90% is obtained by reducing the monoaluminate $Li_2O \cdot Al_2O_3$ in a vacuum (0.1 to 0.5 mm Hg) at 1150 to 1200°.

The direct reduction of spodumene is based on the fact that when spodumene is roasted with lime (CaO) the lime replaces and liberates the lithium oxide; when this process occurs in the presence of a reducing agent, the lithium oxide is reduced to the metal.

The spodumene concentrate is crushed to a particle size of -0.074 mm, mixed with CaO and aluminum or ferrosilicium, and heated to 1050 to 1150° in a special retort in vacuo (10^{-4} mm Hg). The yield of lithium reaches 85%, the degree of purity of the metal is 90%. Because of their high vapor pressure, the potassium and sodium present as impurities are volatilized together with the lithium and collect mainly on the coolest parts of the condenser.

In spite of some advantages of the lithium-manufacturing methods based on thermal reduction with metals (the use of cheap reducing agents, the possibility of producing lithium of a high degree of purity, the possibility of using directly the products of lithium ore dressing or even the ore itself), these methods do not have extensive commercial use; this is due to a certain extent to the complexity of the equipment used for the thermal reduction in a vacuum (as compared with the simpler equipment needed for molten salt electrolysis) and to the extensive use of the molten-salt electrolysis processes.

119. PURIFICATION OF LITHIUM

We mentioned above the rough purification of lithium by remelting under a layer of an inert protective substance, in which the impurities are removed by separation according to their densities. However, the removal of sodium and potassium, whose physicochemical properties closely resemble those of lithium, encounters great difficulties. The main methods used for the fine purification of lithium from these impurities are as follows: 1) hydrogenation of the lithium; 2) refining by distillation at reduced pressures; 3) fractional condensation.

The hydrogenation of lithium is a purification method based on the fact that the hydrides of potassium and sodium are less stable than lithium hydride (decomposition of KH and NaH occurs at 425 to 500° while LiH is decomposed at $\sim$ 1000° in vacuo). To effect the hydrogenation, the lithium is hydrogenated in a current of hydrogen at 700 to 800°, the lithium hydride formed is melted (the melting point of LiH is 690°), and the sodium and potassium (formed in the decomposition of the KH and NaH, which are formed during the hydrogenation) are easily volatilized.

The refining by distillation at reduced pressures (vacuum distillation) is based on the different vapor pressures of lithium, sodium, magnesium and potassium (Figure 229).

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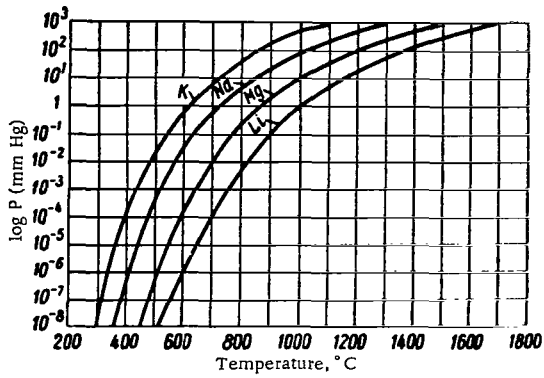

FIGURE 229. Dependence of the logarithm of the vapor pressures of potassium, sodium, magnesium, and lithium on the temperature.

The distillation may be carried out in a steel retort connected to a vacuum system.

The lithium refined at a residual pressure of $4 \cdot 10^{-5}$ mm Hg, at a process temperature of 600 to 800° and a condenser temperature of 340 to 420° contains only 0.001 to 0.003% sodium. The maximum degree of extraction of refined lithium in the condensate is 85 to 90%.

Fractional condensation is based on the different condensation temperatures of lithium, potassium, and sodium; the removal of magnesium by this method is difficult because of the similar vapor pressure of lithium and magnesium.

In addition to the above methods, very thorough purification of lithium (from sodium and potassium) is obtained by zone melting.

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